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CHEMICAL IDENTIFICATION OF THE ODOR COMPONENTS IN DIESEL ENGINE EXHAUST

Final Report (Year 3) to

COORDINATING RESEARCH COUNCIL
and
ENVIRONMENTAL PROTECTION AGENCY

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16. Abstracts The results of a continuing effort to chemically identify the odor components of diesel exhaust are reported. The basic methodology for characterizing and analyzing the diesel exhaust odor was developed during the previous effort on this program. The approach developed involved sensory characterization as an integral part of the study. The experimental approach for analysis of the odor species was to collect large volumes of exhaust by condensation at 0°C, extract the organic portion of the exhaust from the non-odorous portion by liquid column chromatography. During this current program, the details of the methodology required for identification of the smoky-burnt odor fraction were completed and applied to the analysis of this fraction. All of the odor-significant species in this fraction have been identified. While several paraffinic oxidation products were recognized as important odor contributers, the most important smoky-burnt odor species are those associated with the partial oxidation products of compounds found in the aromatic fraction of the diesel fuel.

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I. SUMMARY

A. INTRODUCTION

This report represents the results of a continuing effort to chemically identify the odor components of diesel exhaust. The study is sponsored jointly by the Coordinating Research Council and the Environmental Protection Agency as part of their support of programs designed to obtain a detailed understanding of diesel exhaust and its odor.

The basic methodology for characterizing and analyzing the diesel exhaust odor was developed during the previous effort on this program. (1,2) The approach developed involved sensory characterization as an integral part of the study. The original exhaust odor was characterized as consisting about equally of oily-kerosene and smoky-burnt odors. The experimental approach for analysis of the odor species was to collect large volumes of exhaust by concensation at 0°C, extract the organic portion of the exhaust from the non-odorous portion by liquid column chromatography (LCC). The odorous species separated into two major odor fractions with roughly equal odor intensities -- oily-kerosene and smoky-burnt -- which represented the original exhaust odor.

During the preceding year the principal components responsible for the characteristic oily-kerosene portion of the exhaust odor were identified. Identification of the oily-kerosene odor complex was achieved by resolving the LCC odor fraction using a two-stage gas chromatographic (GC) method and final analysis of the resolved odor species by high resolution mass spectrometry. Using the basic chemical and odor data achieved by analysis of the sample as well as odor studies on selected reference compounds, the chemical classes associated with the oily-kerosene odor complex were found to be: alkyl benzenes, idans/tetralins, and indenes.

Additional sample resolution was required for application of the same methodology used for the oily-kerosene LCC odor fraction to the smoky-burnt fraction. The balance of the preceding year was devoted to developing an improved gradient LCC method for the smoky-burnt odor fraction.

B. RESULTS

During this past year, the details of the methodology required for identification of the smoky-burnt odor fraction were completed and applied to the analysis of this fraction. All of the odor-significant species in this fraction have been identified. While several paraffinic oxidation products were recognized as important odor contributors, the most important smoky-burnt odor species are those associated with the partial oxidation products of compounds found in the aromatic fraction of the diesel fuel.

Of the species identified, the greatest contribution to the smoky-burnt odor character appears to be from the higher molecular weight components and those with multi-functional substitution. Feel factors (irritation, pungency) are frequently associated with the lower molecular weight members of a particular chemical class. Our analysis of this odor fraction was aided by the study of a large number of oxygenated reference compounds, many of which had appropriate odor character and intensity.

In summarizing our odor and chemical identification results for the smoky-burnt odor complex we find that:

- The smoky odor character is most consistently associated with hydroxy and methoxy indanones with some contributions from methyl and methoxy phenols.
- Burnt odors are associated with furans and alkyl benzaldehydes.
- The oxidized oily character is usually ascribed to alkenones, dienones, hydroxy cyclocarbonyls, and indanones.
- Irritation factors seem most frequently to be associated with the lower molecular weight phenols. Some benzeldehydes and methoxy benzenes may also contribute to this sensation.
- While some unsaturated aldehydes contribute to a portion of the exhaust odor complex, the most abundant exhaust aldehydes do not appear to contribute significantly.
- Neither sulfur nor nitrogen containing species contribute to the smoky-burnt odor complex. Although such species were observed during portions of the analyses, none were associated with exhaust odors.

The primary emphasis during the initial phase of the program was on qualitative methods for the identification of specific resolved odorous exhaust species. Emphasis during the balance of the year was placed on development of quantitative methods for the measurement of the identified odorous species. Research was also initiated on the influence of fuel and engine variables on the exhaust odor chemistry. One purpose of these studies is to verify the previous identification data by determining whether any new species are observed under conditions other than the fixed operating conditions, for which the chemical odor data were obtained. A second purpose is to develop a correlation by which one will be able to express diesel exhaust odor by the measurement of selected groups of chemical species.

Various steps of the sample work-up and analysis procedure have been modified so that good reproducibility has been obtained in the measurement of odorous exhaust fractions. A new sample collection procedure which will allow us to work more efficiently with smaller samples of exhaust is being evaluated. Quantitative analysis of each of the major classes of odorous compounds in the oily-kerosene odor fraction has been achieved by application of a computerized matrix analyses of the low resolution mass spectral data for that fraction. An analagous method for representing the relative amount of each of the odorous chemical classes in the smoky-burnt fraction is under study.

Engine and fuel variable studies have been initiated. Preliminary studies show that the analytical fractions accurately reflect the observed change in odor character and intensity with load. Further, some initial data in dicate that measurement of the indan/tetralin group as a total appropriately reflects the level of kerosene odor in the exhaust. Several tentative fuels have been studied in the odor test room for selection of the most appropriate ones for detailed study. An initial examination of the exhaust from a very low aromatics content fuel is encouraging in terms of the correlation between odor and chemical analysis.

C. RECOMMENDATIONS

1. Work on a complete quantitative analytical method for the collection and analysis of diesel exhaust should be completed.

2. Analytical methods should be developed for the analysis of of the aromatic (oily-kerosene) and oxygenated (smoky-burnt) odor fractions in a manner which will reflect the correlation between exhaust chemistry and odor.

3. Study the influence of fuel and engine variables on the nature of the diesel exhaust in detail in order to verify the chemical assignments, provide the variables for establishing a correlation method, and aid in determining the origin of the odor species.

II. BACKGROUND

This section briefly reviews the approach developed during the previous years of our research program.

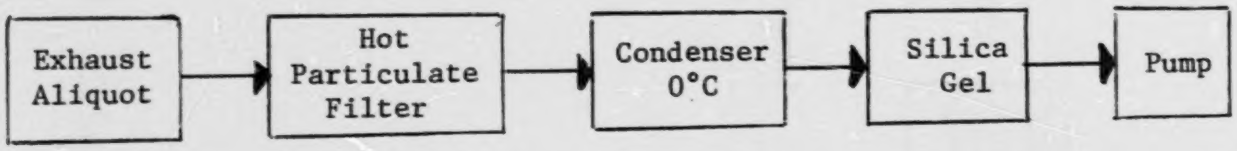
The success of our program is attributed to an approach which combines the sensory talents of odor chemists with the capabilities of analytical chemists to produce a scheme for identifying the trace odor components in the complex diesel exhaust.

The test facility used for these studies is shown schematically in Figure 1. The engine used in these studies is a 71-series 4-cylinder diesel.* For all of the chemical identification work, it has been operated under constant conditions of 1800 rpm and 33% load from a large supply of No. 1 diesel fuel. Fuel and load have been varied for the specific study of these variables. The exhaust from the engine can be passed into an adjacent aluminum-lined test room for sensory evaluation or through a sampling system for collection analysis. A typical odor description using the ADL odor profile method (See Appendix A) is:

TIA**	2
Oily	2
Burnt	2
Kerosene	1½
Eye irritation	✓
Nose irritation	✓
(600/1 dilution)	

Thus, in terms of the overall perception of diesel exhaust odor, the odor quality and intensity is comprised about equally of an oily-kerosene and a smoky-burnt odor complex.

For that portion of the program concerned with chemical identification of the odor components, our preferred sample collection approach is:



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*Detroit Diesel Allison Division of General Motors Corporation, Model 4154N

**Total Intensity of Aroma

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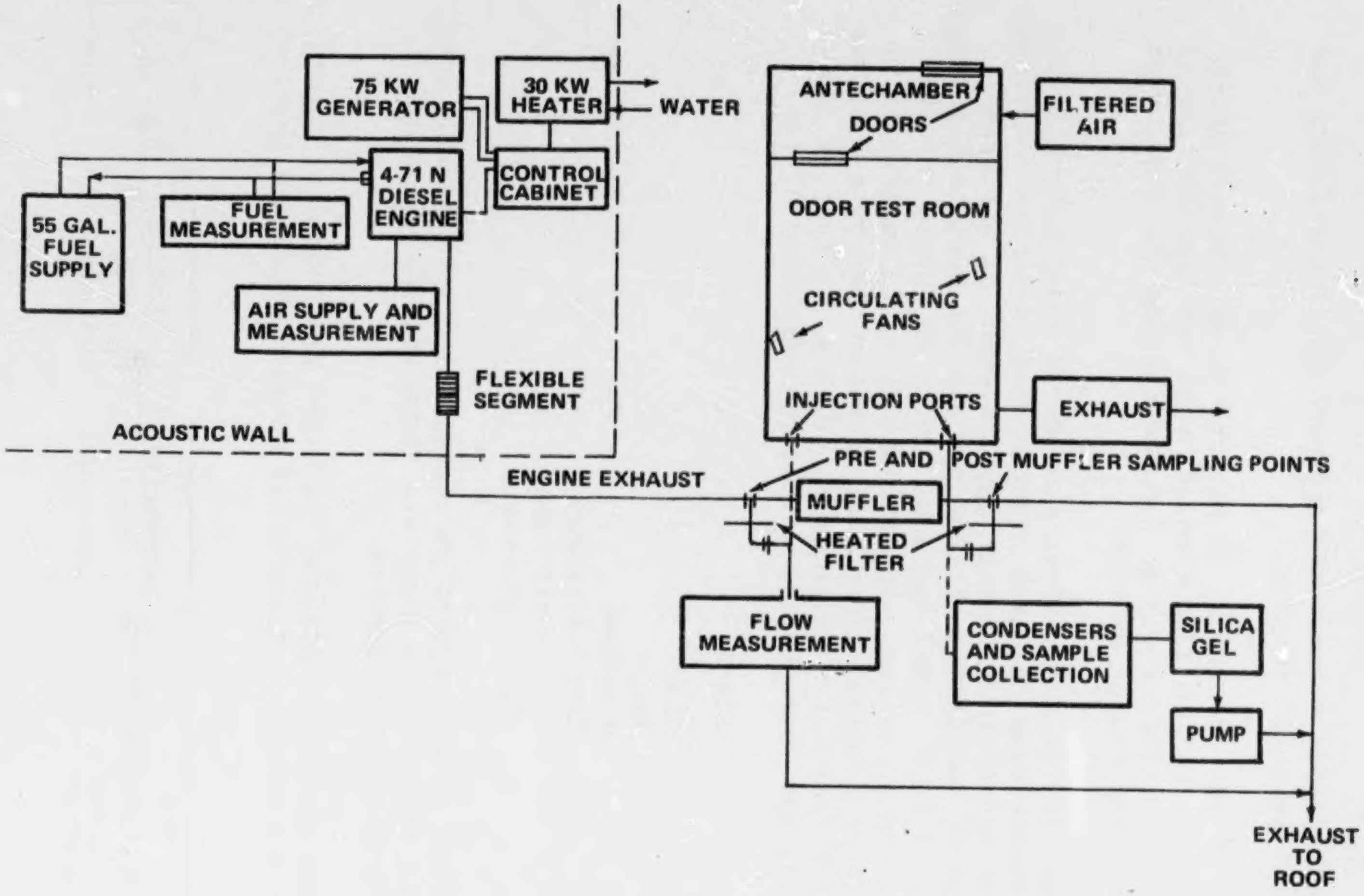

Figure 1 EXPERIMENTAL ARRANGEMENT OF DIESEL ENGINE, ODOR TEST ROOM, EXHAUST SAMPLING AND COLLECTION SYSTEM

Large volumes of the exhaust sample are passed through unheated ½-inch stainless steel pipe, a heated fiber glass filter, and a condenser kept at 0°C. All condensate is collected in a round bottom flask and kept at 0°C. The remaining gases are swept through a silica gel column. Initially, the oirginal system utilizing two Friedrich condensers in series and a diaphragm pump was used to give a sampling rate of about 1000 liters/hour. Later, a high volume sampling system using a single condenser and carbon vane pump was assembled to provide a 10,000 liter/hour sampling rate (See Appendix B.1). Using either method, condensate from 20,000 - 60,000 liters of exhaust was usually collected for the generation of analytical samples.

The standard basic sample workup procedure used for the identification of the oily-kerosene odor fraction is shown in Figure 2 and represents the "normal" distribution of the entire sample. Detailed modifications of this procedure have been made to fit the particular needs of the program, but the procedure still properly reflects the entire process for identification of individual exhaust odor species.

The oil phase which separates from large volumes of exhaust condensate is combined with the pentane and chloroform extracts to provide the concentrated organic portion of the diesel exhaust. This organic concentrate is first separated into major fractions by silica-gel/liquid-column chromatography (LCC) yielding a major non-odorous fraction (LCC-1) and two major odorous fractions - oily-kerosene (fraction LCC-4) and smoky-burnt (fraction LCC-10) (see Appendix C for details of the LCC step). Other non-odorous species in these fractions are separated, and the remaining odorous species are resolved into individual chemical species by two stages of gas chromatography (GC). The first stage uses a silicone column and the second a Carbowax column. The chemical structure of odorous compounds is determined by high resolution mass spectrometry (HRMS). This procedure was used as described for the identification of the oily-kerosene odor species reported in the last final report (2).

The standard LCC procedure as described did not provide sufficient sample resolution for analysis of the smoky-burnt odor complex by the two stage GC-HRMS system. Therefore, a modified sample workup procedure was developed for identification of the odor species in this fraction. The essential changes have been to work up only the chloroform and pentane extracts of the aqueous condensate independently and separate the odor fractions utilizing a more detailed LCC gradient elution. These modifications are shown schematically in Figure 3. Using the modified procedure a gain of a factor of 5-10 in the odor/mass ratio was obtained in the eluted smoky-burnt odor fractions compared with the standard procedure are given in Appendix C.2.

Throughout the program, we have depended on the odor profile technique to determine whether samples of diesel exhaust maintained their odor character after each analytical step.

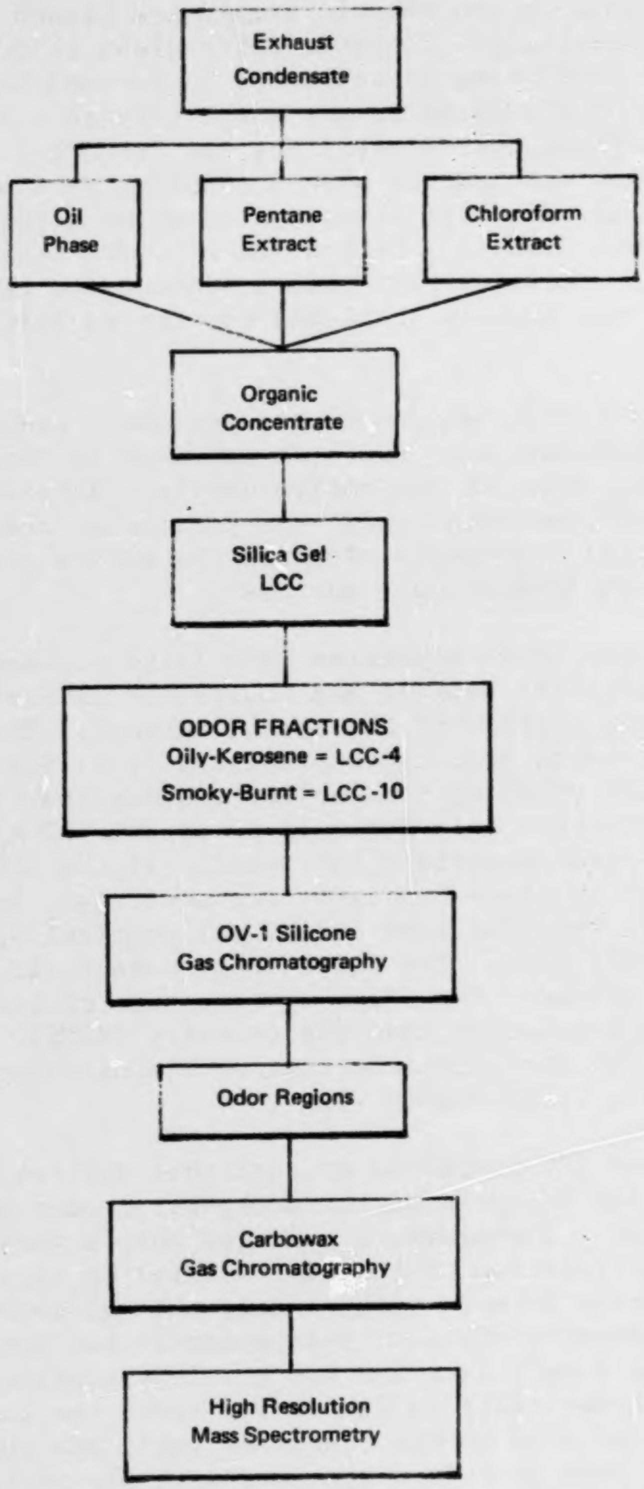

FIGURE 2 STANDARD DIESEL EXHAUST WORKUP PROCEDURE

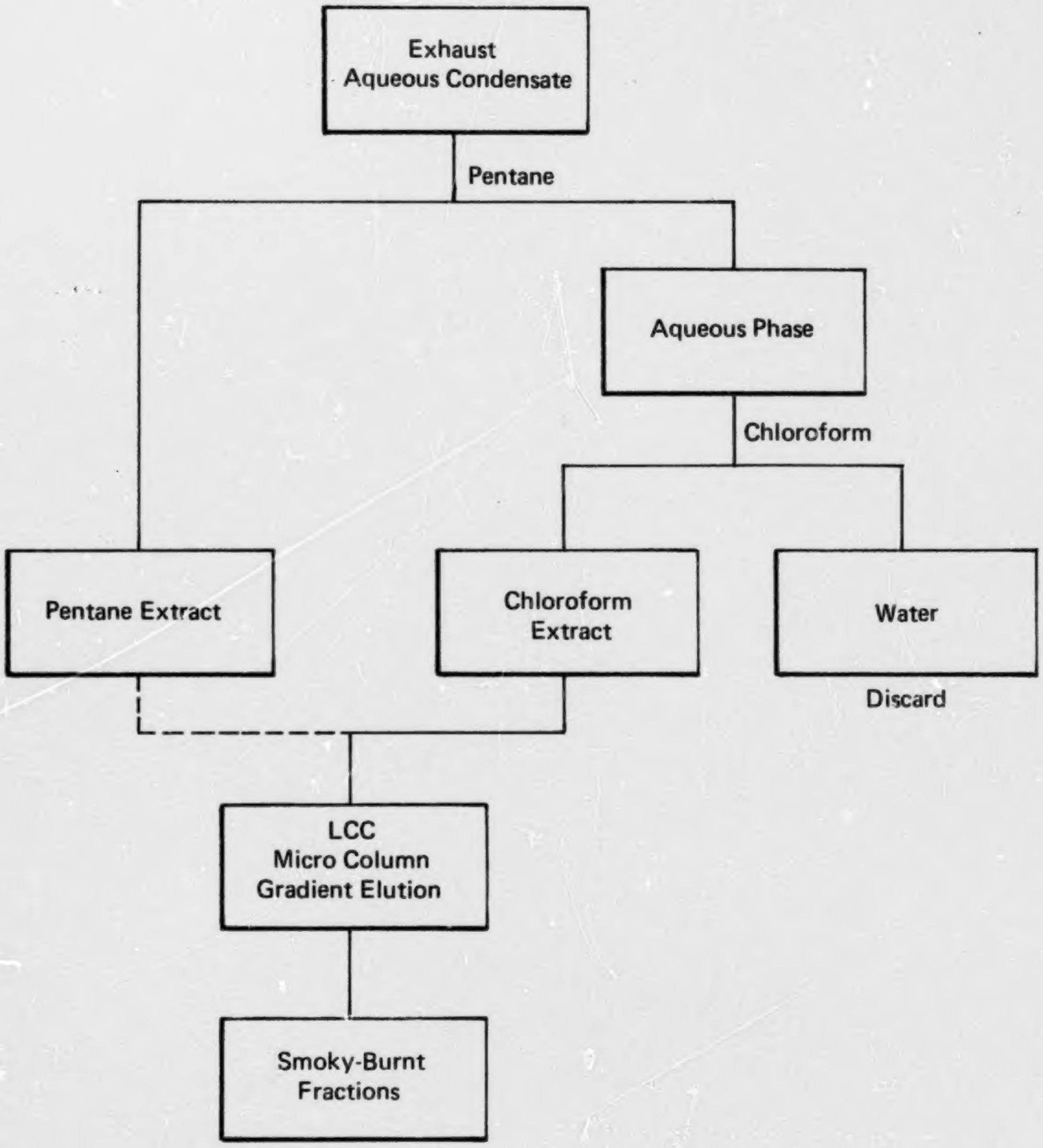

FIGURE 3 MODIFIED SMOKY-BURNT ISOLATION SEQUENCE

III. CHEMICAL IDENTIFICATION OF THE SMOKY-BURNT ODOR COMPLEX

The basic scheme described in "Background" using the modified separation procedures has been applied to an identification of the major species contributing to the odor of the smoky-burnt diesel exhaust fraction.

A. SAMPLE PREPARATION

Four separate collections of large volumes of diesel exhaust were made to complete this portion of the project. Samples 51 and 52 (45,000 liters each) were collected with the original 1000 liter/hour trapping system. Samples 56 and 60 (50,000 liters each) were collected with the new high volume sampler designed to increase the experimental efficiency (see Appendix B.1 for details). The modified sequence used for identification of the smoky-burnt odor species is represented completely in Figure 4.

Earlier work had shown that virtually all of the oily-kerosene odor species in the exhaust condensate were extracted by the pentane and chloroform extracts. Because of its more favorable odor-to-mass ratio, identification of the smoky-burnt odor species was completed by working primarily on the chloroform extract of the condensate. Sufficient research was done on the pentane extract portion to obtain the contribution of the odorous compounds present in that extract to the total smoky-burnt exhaust odor.

The chloroform extracts from each of the sample collections and the pentane extract from sample 56 were subjected to the gradient elution LCC procedure described in Appendix C.2. The identification results are thus based on the analysis of four separate exhaust sample, namely:

Chloroform Extracts

Sample 51C	fractions 34/35
Sample 52C	fractions 34/35/36 + sample 56C fractions 39/40
Sample 60C	fractions 39/40/41

Pentane Extract

Sample 56P	fraction 40

These samples appeared to be consistent with all of our earlier observations, and we feel that they accurately reflected the important smoky-burnt odor fractions of the original diesel exhaust.

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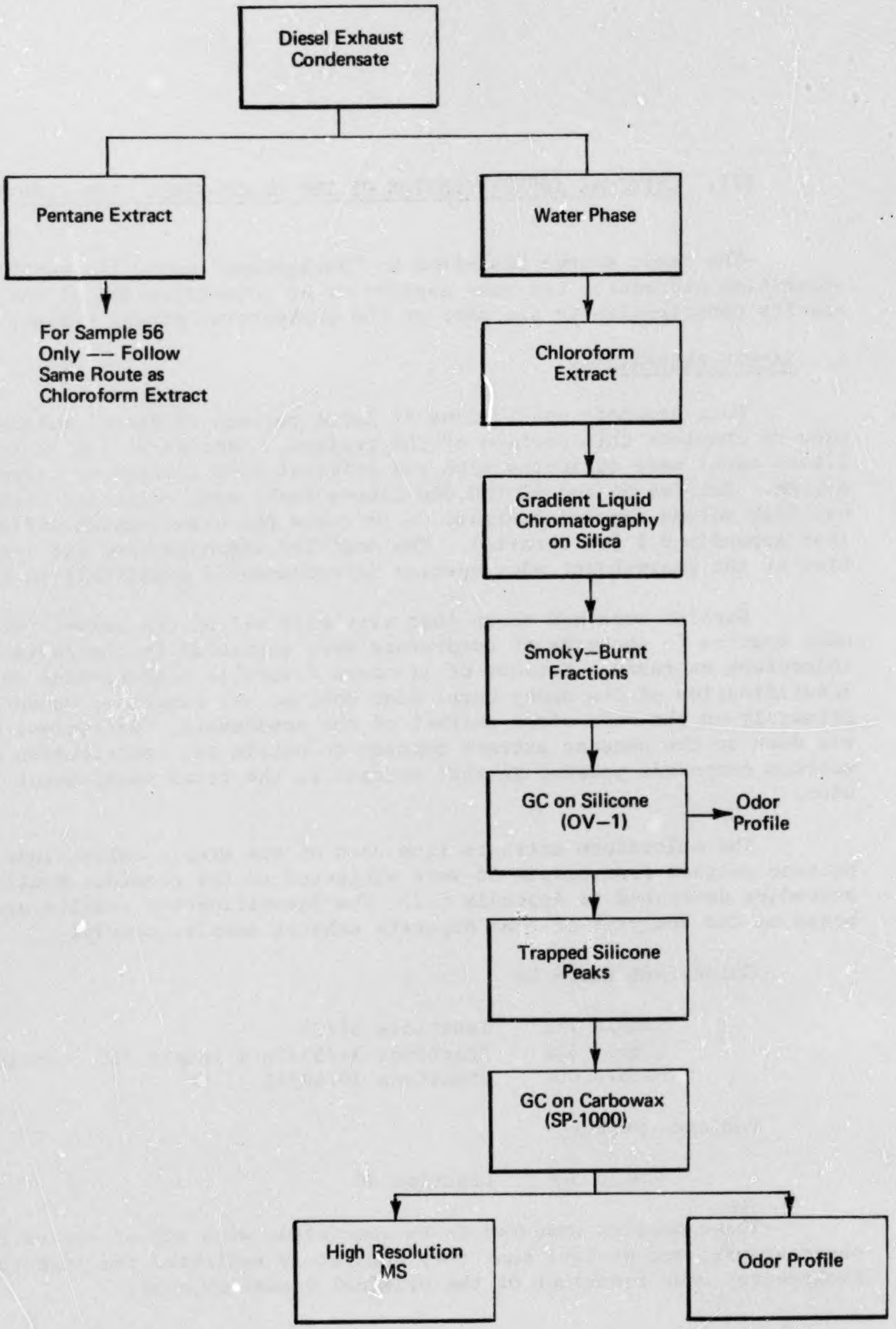

FIGURE 4 PROCEDURE FOR ISOLATION AND CHARACTERIZATION OF THE SMOKY–BURNT FRACTION

B. GAS CHROMATOGRAPHIC SEPARATION AND RESOLUTION

Our previously developed techniques were used for the final isolation, odor characterization and chemical identification of individual smoky-burnt odor species (see Ref. 2). Thus, odor profiles were determined on the samples described above after gas chromatographic resolution on an OV-1 silicone column. The most significant odor areas were defined and then designated for trapping and further resolution. Trapping of the selected areas was done using short lengths (1/8" x 5") of stainless steel tubing containing OV-1 column packing at room temperature. Then, the trapped areas were rechromatographed on an SP-1000 Carbowax column (Supelco Company). The SP-1000 column is a significant improvement over previous Carbowax columns allowing components to elute at about a 50°C lower temperature and showing four to five times less column bleed at 200 - 250°C.

Initial studies on Sample 51C were done using one aliquot for GC-odor and a second for GC-MS. The experimental procedure was then modified to improve reliability and sample efficiency and the remainder of the studies were carried out with the SP-1000 GC effluent split three ways to allow simultanelus GC-Odor-HRMS studies. All of the pertinent chromatograms that we obtained during this work have been included in Appendix D. The silicone chromatograms for each sample appear first, followed by the Carbowax chromatograms of each trapped peak.

C. CHEMICAL IDENTIFICATION OF ODOR SIGNIFICANT SPECIES

High resolution mass spectra (HRMS) were obtained on each of the species eluting from the Carbowax column which were considered to be significant odor contributors. These data provided the basic information for assignment of chemical structures to specific exhaust odor compounds. However, wherever possible the structural assignments were also made by correlations developed by the study of reference compounds and full application of all of the available odor and gas chromatographic retention data. A detailed discussion of the methodology used is presented in Appendix E. The basic data derived from the studies are summarized in Appendix F. These data include reference to the original silicone peak which was trapped and its nominal OV-1 elution temperature, the Carbowax temperature program conditions used, and elution temperature, the photoplate exposure number (peak number), the odor descriptors, and the HRMS data for the parent molecular ion.

In addition, the approximate percentage of the individual components in the total samples have been estimated qualitatively along with possible structure type assignments for most of the observed species. In a few cases chemical structural assignments are definite (where indicated), but for most of the species the structures assigned represent our best present estimate of the probable chemical class.

As described in Appendix E, one of the most useful ways we have found for organizing these data is by means of the rings plus double bonds (R+DB) classification system (3), a means of representing the structure of a compound by means of its hydrogen unsaturation. Appendix G presents the data for the smoky-burnt fraction according to an organization based on the R+DB values observed for each identified odor species.

D. STUDIES ON REFERENCE OXYGENATED COMPOUNDS

The high degree of similarity in the basic fragmentation behavior of some of the phenols, benzaldehydes, indanones, and indanols in particular has made it difficult to clearly distinguish between them on the basis of the mass spectrometry data alone. Therefore, the attempts to assign structure types have been considerably aided by a study of the GC behavior of reference compounds on the silicone and Carbowax columns. The retention data on the 144 oxygenated reference materials studied to date are listed in Table H-1 of Appendix H. The GC data have been extremely useful in placing limits on structural considerations and in establishing correlations between structure types.

Several of the reference compounds were also studied in the odor test room (Table H-2, Appendix H) for further confirmation of the consistency of the chemical structure/odor assignments. The phenol-based materials tend to smell medicinal, but as alkyl substituents are added they appear to be more reminiscent of odors observed in diesel exhaust. Several of the benzaldehydes and indanones (tetralones) have odors consistent with portions of the smoky-burnt odor complex. The concentrations at which the model compounds are detectable in the test room are consistent with the concentrations of compounds observed in the diesel exhaust fraction.

E. DISCUSSION OF RESULTS

Using the program described above, we have accumulated a wealth of data -- odor evaluation, gas chromatographic retention behavior, and high resolution mass spectrometric composition -- on the smoky-burnt odor complex. This section will present the important highlights of the work, while the specific odor composition details can be found primarily in Appendices F and G.

In attempting to describe the state of our knowledge, it is important to stress that there are several levels of confidence that can be assigned to various segments of the data. We feel very strongly that we have developed a basic understanding of the types of compounds in diesel exhaust which cause the smoky-burnt character of the total odor. In some cases, we also have identified specific compounds within a compound class. However, most of the specific compound identification assignments are tentative. We intend to continue firming up these individual assignments, but we do not feel that changes in identification of specific chemicals will have any significant impact on the course of the total program beyond adjusting our thinking in quantitative terms. Therefore, we are proceeding on to other phases of the study and continuing the identification studies at a low level of effort.

Based on the original diesel exhaust odor characteristics (oily, kerosene, smoky-burnt, and irritation factors) our primary concern has been to identify components which are recognizable in the exhaust as smoky character notes and secondarily as burnt character notes. There is some interest in oily or oxidized oily notes as well as sour, leather, linseed, and naphthenate descriptors. Each of these are detectable at varying times in some of the liquid column chromatography fractions. In addition, the added resolution obtained by the first and second stages of gas chromatography permits one to recognize a great variety of odor characteristics. The latter problem taxes the observers' descriptive language and confuses his ability to recognize characteristics because of the variety of rapidly appearing and changing odors. The goal of the odor analyst during this phase of the work is to recognize and indicate only those odor components which are most importantly associated with the original odor profile.

We have found in this program that many of the same types of chemical structures appear to relate to different aspects of the odor. Some of this redundancy undoubtedly is real -- but considering the difficulties facing the odor chemist some may represent interference during the odor examination.

The chemical and odor observations on the smoky-burnt fraction are summarized in Table 1. This table lists the approximate percentage for which each structure class was observed in the chloroform (C) and pentane (P) extracts, as well as showing that the total amount of the measured species account for approximately 20% of each of the extracts. We believe that much of the remainder of the extract is represented by similar materials which we did not happen to measure. In addition, there undoubtedly are also several types of species, such as some residual alkyl benzenes and naphthalenes which account for some of the mass but do not contribute to the odor. This list provides the major structure classes, which are primarily alkyl-substituted species. The generic name also includes the hydroxy and methoxy derivatives of these classes. The "carbon range" column indicates the range of carbon numbers which we observed for each of the classes.

The odor intensity and character notes of the chloroform and pentane extracts were found to be different. In the chloroform extract, a complex of smoky-burnt is the major odor. This is supported by character notes described as oxidized oily, sour and naphthenate, and detectable levels of a sensory impression of irritation or pain. In the comparable pentane extract, the odor mixture is more complex and consists of kerosene-related odors, which are dominant, with supporting notes of oily and burnt smoky.

In conjunction with these odor differences, a comparison of the chemical data obtained from the chloroform and pentane extracts revealed that the initial exhaust condensate extraction process was somewhat selective. There is a greater abundance of the more polar species in the chloroform sample, such as the phenols and hydroxy/methoxy indanones, while the less polar materials such as the dienones are found preferentially in the pentane extract. Even in cases where phenols, for instance, were isolated in both fractions, the pentane extract tends to contain the less polar homologs as indicated by their earlier elution from the Carbowax GC column (see appendix F for details).

TABLE 1

Smoky-Burnt Summary Observations

--- %[b] ---					
C	P	Structure Class[a]	R + DB[c]	C Range	Principal Odor Contribution
1.0	1.1	Alkenone	2	C_5-C_{11}	Oxidized oily
1.0		Furan	3	C_6-C_{10}	Irritation, burnt
	1.4	Dienone	3	C_9-C_{13}	Sour, oxidized oily
0.9		Furfural	4	C_6-C_7	Burnt, oily
0.7	0.1	Methoxy benzene	4	C_8-C_9	Smoky, pungency
4.9	1.0	Phenol	4	C_7-C_{12}	Burnt, irritation, tarry, particle size
2.7	6.8	Benzaldehyde Phenyl ketone	5	C_7-C_{13}	Burnt, pungency
1.6		Benzofuran	6	C_8-C_9	Particle size
6.1	2.2	Indanone (plus indenols)	6	C_9-C_{13}	Metallic, smoky, sour
1.0	1.6	Indenone	7	C_9-C_{14}	Leathery, tarry, burnt
0.4	4.9	Naphthaldehyde	8	C_{11}-C_{12}	Particle size

---

a. includes hydroxy and methoxy derivatives, most with alkyl substitution.

b. percent of each class in the chloroform (C) and pentane (P) extract.

c. see Appendix E for discussion of R + DB.

Summarizing this another way:

- Hydroxy and methoxy indanones are most consistently described as smoky, while methyl and methoxy phenols may also contribute to this character note.
- Burnt odors are associated with components described as furans and possibly alkyl benzaldehydes and acetophenones.
- The oxidized oily character note is usually ascribed to alkenones, dienones, hydroxy cyclocarbonyls and indanones.
- Irritation seems to be most frequently associated with the lower molecular weight phenols. Some of the alkyl benzaldehydes and methoxy benzenes may also contribute to this sensation.
- Odor observations consistently seem to indicate that the feel factors (pungency, irritation) are associated more with the lower molecular weight members of a class, and the odor character is associated with the more highly substituted or more poly functional derivatives.

The HRMS data acquired for all of the odor significant peaks has also been examined in an effort to determine whether sulfur or nitrogen-containing compounds are present in any of the areas we have examined. We were unable to find any such species in the data. We consider this observation to be significant in view of the fact that we were able to detect species present in the exhaust at about 1 ppb and based on odor threshold data would have observed the species if they had contributed to the odor.

Finally, several quantitative studies were carried out with reference compounds to determine whether any major odor components of the smoky-burnt complex could have been lost in the liquid column and gas chromatographic steps. The studies show good material recoveries and indicate that it is unlikely that any important odor species were selectively lost in the procedures.

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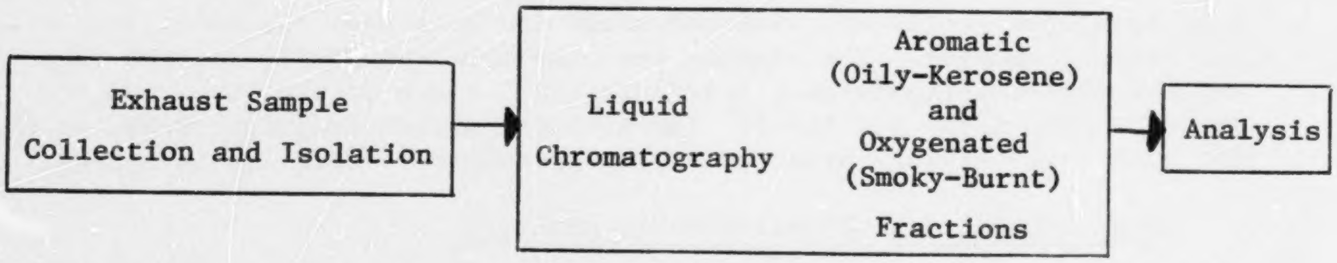
IV. QUANTITATIVE ANALYSIS METHODS

The next phase of our research program involves a study of fuel and engine variables. The purpose of these studies is to determine the completeness of our chemical structure/odor assignments to date and to provide the variation in exhaust data by which correlation schemes between composition data and odor may be evaluated. The analytical approach used for the identification phase is usable for initiating these studies, but the approach is complex and time-consuming and not designed primarily for repetitive use.

We have, therefore, initiated a study to develop a simpler (but not a "Black Box") quantitative method which will be appropriate for use first in our own laboratories for expediting the variables study and ultimately in other research laboratories. Each step in the procedure is being studied in detail. This portion of the study is still in progress and results in some areas are still in the tentative stage.

The overall scheme under study involves



and basically eliminates the gas chromatography steps for the final analysis. The scheme continues to rely upon liquid chromatography as the most effective means of separating the odorous and non-odorous compounds and providing odor fractions which are directly amenable to analysis by mass spectrometry. Individual studies to date on each of these steps are discussed in the following sections.

A. EXHAUST SAMPLE COLLECTION

Although the condenser systems used for the study to date are effective in obtaining a representative portion of the diesel exhaust, we have known for some time that the exhaust odor is not collected quantitatively by that method. We had observed earlier that a bed of silica gel placed after the condenser was effective in removing all of the diesel exhaust odor.

We have begun to explore means of collecting samples by direct adsorption on substrates such a silica gel. Our studies to date on silica gel itself are quite encouraging and suggest that this approach will ultimately provide the preferred method. The method is described in detail in Appendix B.2.

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Approximately 720 liter samples of diesel exhaust have been collected directly on 25 grams of silica gel over a one-hour collection period. We have found that the odorous exhaust species can be effectively removed from the silica gel by a pentane/acidic methanol elution.

For the 33% load engine condition, the total organic extract (TOE) obtained by this method was approximately 250-300 mg/Kℓ of exhaust. These data contrast with an average 15-25 mg/Kℓ obtained with the condenser system. Thus, an order of magnitude gain has been made in sample collection efficiency. Significantly, the total extract from the gel trapping method, when examined in the odor test room at an equivalent of 21 liters of exhaust, has an odor intensity and quality which is nearly the same as a direct 21 liter of exhaust sample.

This new collection procedure is much more efficient than the condenser systems as well as meeting the quantitative requirements of the overall program. Further, since the odor fractions will initially be analyzed as a total group only, 500-1000 liter samples of exhaust are sufficient.

B. LIQUID CHROMATOGRAPHY

A micro version of the standard liquid chromatography procedure has been developed consistent with the needs for analyzing the 1000 liter silica gel trapped samples. The elution sequence has been simplified and established so that the odor-significant fractions still elute in the LCC-4 (oily-kerosene aromatics) and LCC-10 (smoky-burnt oxygenates) fractions, as they did under the original procedure. The procedure is detailed in Appendix C.3.

C. TOTAL ORGANIC GAS CHROMATOGRAPHIC ANALYSIS

The basic preliminary analytical data we wished to obtain was the total organic mass found in the solvent extracts and the LCC fractions. We had previously obtained these data from the temperature-programmed GC analysis on the ten-foot silicone column. This method had the problem that it was time-consuming for the data desired and difficult to measure the eluting area since the base line was sometimes difficult to define. Therefore, a new assay procedure was developed using a short column and rapid temperature programming.

The column is a 1½' x 1/8" stainless steel column packed with the same 10% OV-1 used previously and used in our P-E 900 with FID detection. The column is maintained at ambient temperature for three minutes to allow the solvent to elute and then heated ballistically to 250°C over a three-minute period. During this heating period, the sample elutes as a relatively unresolved peak which is well defined and easy to measure quantitatively. All total mass data have since been obtained by this method. The reproducibility of the assay is acceptable, as can be seen in the data shown in Table 2, which was obtained by repeated analysis of the same samples on the dates shown.

Table 2

Reproducibility of Total Organic GC Method

Date	Fuel Oil Response (sq. in/μg)	Total Organics[a] Observed in: Pentane Extract (62-P)	LCC-1 (64-LCC-1)	LCC-10 (64-LCC-10)
12/18/70	27.1	50.4	9.1	1.40
12/23/70	30.7	45.7	8.0	1.40
12/29/70	26.6	52.8	11.1	1.34
1/5/71	27.1	49.4	8.6	1.05
1/14/71	24.5	-	11.5	1.24
Average	27.2±3.5	49.6±4.0	9.7±1.8	1.29±0.24

[a] mg/1000 ℓ as FOE values

At the present time we are still using diesel fuel to calibrate the flame response to obtain weights (as FOE, Fuel Oil Equivalent) of all the silica fractions. If an appropriate mixture can be found, we may use separate calibration mixtures for the paraffin, aromatic, and oxygenate fractions. The error, however, introduced by using fuel for all fractions is minor.

D. ANALYSIS OF CHEMICAL CLASSES

1. Aromatics -- Oily-Kerosene Odor Complex

According to the chemical identification/odor data described in the second final report (2), a measurement of the indans and tetralins present in the exhaust samples should provide a measure of the kerosene odor note while the alkyl benzene concentration should reflect the oily note.

The most efficient means of obtaining those data at the present time is by means of a low resolution mass spectral analysis of the LCC aromatic fraction. The petroleum industry has developed computer programs for the matrix analysis of such aromatic fractions and the version developed by the Mobil Research and Development Corporation was kindly supplied to us for our studies. The Fortran program has been converted to process data on our laboratory Hewlett-Packard 2116B computer. A typical analysis of a condensate LCC-4 oily-kerosene aromatics fraction derived from the No. 1 diesel fuel looks like:

Sample: Experiment 66 LCC-4

Class	%
Alkyl benzenes	23.6
Tetralins, indanes, indenes	14.2
Naphthalenes	57.1
Acenaphthenes, fluorenes, etc.	4.6
Phenanthrenes, anthracenes, etc.	0.4

The exhaust and fuel samples from the No. 1 diesel fuel do not normally have a significant amount of the last two classes. These classes are important, however, in higher boiling fuels and may reflect additional odor character notes.

This form of data analysis basically provides a fairly rapid means of estimating the idan/tetralin concentration in odor samples to determine the degree of correlation between composition and odor. We have just begun to examine the correlation data and will need to study more samples derived from various load and fuel conditions to fully assess the appropriateness of this approach.

2. Oxygenates -- Smoky-Burnt Odor Complex

It is much more difficult to begin to establish an assay method for the smoky-burnt odor than the oily-kerosene odor species for several reasons. First, there appear to be five to seven general compound classes we wish to measure out of a total of about twelve -- versus two out of three for the aromatics, and many of these have overlapping group functionality. Secondly, we have not yet progressed to the point that we know with the certainty that was established for the oily-kerosene species just what classes we primarily wish to measure. Finally, the detailed isomeric and functional group choices of many species have not yet been verified, and the compounds are only known with certainty by their mass spectral and chromatographic data. For these reasons and the reason of efficiency in using the same technique for analysis of both odor fractions, we have begun to explore in a preliminary way the suitability of mass spectrometry for analysis of the smoky-burnt odor classes.

Examination of the odor-chemical structure data indicates a preliminary first choice of wishing to measure alkenones and furans (R+DB 2,3) for oxidized oily, and phenols (R+DB 4), benzaldehydes (R+DB 5), and indanones and tetralones (R+DB 6) for the burnt and/or smoky odor components of the LCC-10 exhaust fraction. We have examined both the high and low resolution mass spectra of LCC-10 fractions to determine whether data reflecting the concentration of these classes could be obtained in a manner similar to the aromatics program.

Upon examination of the data we find that the intensity of many of the significant mass values for these species in the low resolution spectra is contributed to substantially by the spectrum of ions with an aromatic composition, and there is a great deal of fragmentation leading to similarities from different chemical classes. A typical example is the distribution of compositions found by high resolution at mass 132, the parent ion mass of indanone:

Relative Intensity	Precise Mass	R+DB	Composition
20	132.0452	2	$C_5H_8O_4$
60	132.0560	6	C_9H_8O
20	132.0808	1	$C_6H_{12}O_3$
50	132.0939	5	$C_{10}H_{12}$

We have also examined the spectra at low ionizing voltage (15 ev, compared to the normal 70 ev) in the hopes of enhancing the more easily ionized oxygenated species. Although the overall degree of framentation has decreased somewhat under these conditions, and the spectrum somewhat simplified, the results still did not improve sufficiently to enable us to use the low resolution approach.

In the course of this analysis, however, it did become apparent that the complete high resolution mass spectra contained all the information one needs for this interim analysis period. The data provides the potential for highly refined compound class analysis to test various chemical class-odor correlations through application of proper computerized manipulation of the data. A small effort has been put into some preliminary computations, and the results and future potential appear very attractive.

For instance, since the chemical composition data are completely resolved by virtue of the exact mass differences between various compositions, it is a simple matter to instruct a compilation of all desired oxygenated species. Similarly, one can organize particular data in various formats to explore the potential of conducting the analysis in that manner.

In some preliminary attempts, the smoky-burnt oxygenated fraction has been organized by R+DB value to list all appropriate molecular ions based on the identification data. The compilation routine was instructed to exclude complicating data such as hydrocarbons, ^{13}C isotope peaks, fragment ions (odd mass), and all ions less than mass 94, the lowest molecular weight observed in any of the identified exhaust species. Table 3 shows examples of the output obtained for three of the odor significant R+DB classes from an exhaust condensate LCC-10 smoky-burnt sample.

The tables list the intensity (HGT) of each ion relative to the most abundant ion in the entire spectrum, the precise mass (DET. MASS), calculation error in millimass units (0.3 = 0.0003 mass units), the R+DB value, a value X to be ignored, and the elemental composition.

The R+DB 2 (DB = 2) class represents the alkenones and hydroxy alkenones associated with the oxidized oily odor note, while the R+DB 4 class represents primarily phenols. The R+DB 6 class represents indanones associated with the smoky and burnt odors.

After examining several sets of data in this manner, the potential looks very good for obtaining detailed analysis of the smoky-burnt mixture in this manner with a minimum investment in effort.

As the odor correlation develops and we learn more precisely what chemical classes we wish to measure, it may be appropriate to develop alternative means of more directly measuring those species. It certainly is a requirement of a simpler analytical method to be used in other laboratories. However, at the present time this approach appears to offer the maximum potential for obtaining detailed quantitative data from a very complex sample based on the sample chemistry. Further refinements will be made in the analysis scheme as the rationale develops.

Table 3

Examples of an R+DB Analysis of the Smoky-Burnt High Resolution Mass Spectral Data

```
ANALYSIS FOR DB=    2

            HGT     DET. MASS ERROR  R+DB   X      C12C13   H   O


             5       93.07135 -1.82  2.00   2        6   0  10   1
             2      100.05058 -1.84  2.00   2        5   0   8   2
             3      112.08746 -1.36  2.00   2        7   0  12   1
             2      114.06662 -1.45  2.00   2        6   0  10   2
             2      126.10253 -1.93  2.00   2        8   0  14   1
             1      128.08229 -1.44  2.00   2        7   0  12   2
             1      140.11868 -1.44  2.00   2        9   0  16   1
             1      142.09842 -0.96  2.00   2        8   0  14   2
             1      156.11438 -0.65  2.00   2        9   0  16   2


 SUM HGT =    18


ANALYSIS FOR DB=    4

            HGT     DET. MASS ERROR  R+DB   X      C12C13   H   O


             6       94.04069 -1.18  4.00   6        6   0   6   1
             3       96.01967 -1.46  4.00   6        5   0   4   2
             7      108.05635 -1.16  4.00   6        7   0   8   1
             5      110.03608 -0.70  4.00   6        6   0   6   2
             6      122.07203 -1.14  4.00   6        8   0  10   1
             4      124.05181 -0.62  4.00   6        7   0   8   2
             1      126.03078 -0.91  4.00   6        6   0   6   3
             3      136.08742 -1.40  4.00   6        9   0  12   1
             3      138.06667 -1.41  4.00   6        8   0  10   2
             1      140.04692 -0.42  4.00   6        7   0   8   3
             2      150.10326 -1.20  4.00   6       10   0  14   1
             2      152.08291 -0.81  4.00   6        9   0  12   2
             1      154.06278 -0.21  4.00   6        8   0  10   3
             1      164.11939 -0.72  4.00   6       11   0  16   1
             1      166.09858 -0.80  4.00   6       10   0  14   2
             1      178.13464 -1.12  4.00   6       12   0  18   1
             1      180.11450 -0.52  4.00   6       11   0  16   2
             1      192.15108 -0.34  4.00   6       13   0  20   1
             1      194.13053 -0.15  4.00   6       12   0  18   2


 SUM HGT =    50
```

Table 3 (cont.)

```
ANALYSIS FOR DB=    6

           HGT     DET. MASS ERROR   R+DB   X      C12C13  H   O


            3     104.02553 -0.68   6.00 10          7   0   4   1
            6     118.04173 -0.13   6.00 10          8   0   6   1
            1     120.02079 -0.34   6.00 10          7   0   4   2
            8     132.05617 -1.34   6.00 10          9   0   8   1
            5     134.03526 -1.52   6.00 10          8   0   6   2
            1     136.01536 -0.68   6.00 10          7   0   4   3
            9     146.07152 -1.65   6.00 10         10   0  10   1
            8     148.05127 -1.16   6.00 10          9   0   8   2
            3     150.03085 -0.84   6.00 10          8   0   6   3
            8     160.08803 -0.79   6.00 10         11   0  12   1
            4     162.06723 -0.85   6.00 10         10   0  10   2
            2     164.04679 -0.55   6.00 10          9   0   8   3
            3     174.10380 -0.67   6.00 10         12   0  14   1
            2     176.08301 -0.71   6.00 10         11   0  12   2
            1     178.06112 -1.88   6.00 10         10   0  10   3
            1     188.11954 -0.58   6.00 10         13   0  16   1
            1     190.09878 -0.60   6.00 10         12   0  14   2
            1     202.13531 -0.45   6.00 10         14   0  18   1

 SUM HGT =    67
```

V. VARIABLES STUDY

The study of engine and fuel variables became a major portion of our research effort during the last part of the program. The primary objectives of these studies are to develop the chemical class-odor correlation necessary for instrumental measurement of diesel exhaust odor and to verify and determine the completeness of the identification data obtained to date under our fixed operating conditions.

These studies are still in the preliminary stages. Out initial objectives have been to examine the exhaust and analytical fractions derived from the exhaust under the variable conditions to determine how the exhaust odor is reflected in the separated odor fractions, both qualitatively and quantitatively. Then each primary odor fraction will be analyzed according to the procedures described in Section IV D. Our first effort will be to determine the quantitative correlation between chemical composition and odor in the resolved fractions. Once this correlation is achieved, an effort will be made to establish the same type of correlation in the total organic extract of the diesel exhaust.

A. ENGINE LOAD

1. Exhaust Odor

The effect of engine load on exhaust odor has been studied in detail by examining the exhaust produced with the engine at 10, 33, and 90% load operating at a constant 1800 rpm, using the No. 1 diesel fuel. Some relevant experimental engine operating parameters for these load conditions are given in Table 4.

Odor profile composites for the three load conditions (10%, 33% and 90%) appear in Table 5. These profile descriptions represent a summary of the results of numerous studies at each of the load conditions. The terminology is selected to best represent the consensus of the panel description as well as to differentiate the character of the three load conditions.

The 33% load used for all of the former chemical identification studies has a moderate total intensity of aroma, which is easily recognized in the test room and described in general as diesel exhaust. The primary characteristic as previously noted is the smoky-burnt character note at a moderate intensity. This is supported by an oily odor described as oxidized. The kerosene odor note is the third descriptor in the profile which, from our previous work, was shown to be associated with aromatic hydrocarbons. This note appears to vary somewhat from sample to sample in intensity, either because of concentration or as a result of odor blending. The feeling sensations are primarily nose irritation (a stinging or pain sensation in the nose) and some slight eye irritation.

Table 4

Engine Operating Parameters Under Various Load Conditions[a]

Load (%)	Exhaust Temperature (°F)	Fuel Consumption (Kg/hr)	Collected water[b] ml/1000ℓ
10	290	5.5	4.7
33	380	8.2	15
90	615	14.6	29

a. No. 1 Diesel Fuel, 1800 rpm.

b. Average amount of water collected/1000ℓ of exhaust by high volume condenser sampling systems.

TABLE 5

EXAMINATION OF DIESEL EXHAUST ODOR AT VARIOUS LOADS[a]

10% Load		33% Load		90% Load	
TIA	2	TIA	2	TIA	2
Burnt-smoky	2	Smoky-burnt	2	Smoky-tarry	2
Sour oxidized oil	1½-2	Oily (oxidized)	1½	Hot oily	1½
Kerosene	½-1	Kerosene	1-1½	Metallic (acrid)	1½
Sooty particle feel		Nose irritation	✓	Nose irritation	✓✓[b]
Eye irritation	✓	Sl. eye irritation		Headache	
Nose irritation	✓				

a. 20 liter samples
b. ✓✓ = more intense than ✓

In comparison at 10% load, although the total intensity of aroma is still moderate, a sour oxidized oily character note appears to be of primary importance. The smoky-related character note which remains as the most intense odor is somewhat sweeter and described as burnt-smoky to contrast with smoky-burnt. The kerosene odor notes are less apparent than at 33% load, varying between a just perceptible and a slight intensity. In addition to the sweetness of the burnt-smoky descriptor, there is a sooty, almost particular, feel which appears to be characteristic of the 10% load. This is evident both in filtered and nonfiltered exhaust samples. Irritation appears to affect the eyes as much or more than the nose under this load condition.

With 90% load, although again the total intensity of aroma is moderate, it seems to be fuller and heavier, possibly associated with higher molecular weight oxygenated compounds. The smoky character note is further described as tarry to indicate this increased heaviness and fullness. Under these conditions, the oily aroma is qualitatively quite different from the 10% load and is described as hot lube oil rather than as sour or oxidized. This appears to be consistent with the change observed by the increasing load situation noted from 10% to 33% load. At 90% load, the panel does not describe kerosene or fuel-related odors, but the term "hot metal", "stove pipe" or "metallic-sharpness" is noted which may relate to an acrid or pungent character of the exhaust.

The nose irritation at 90% load appears to be the highest of the three conditions examined. There are in addition occasional references to headache produced with 90% load condition which is not generally recognized at the lower load conditions. This is often perceived as pain just behind the eyes.

2. Chemical Analysis of Exhaust Samples

Several initial sample collections and fraction odor evaluations were made at the three load conditions using the condenser sampling system in order to initiate our studies in this area. These studies were described in the third quarterly progress report. Since the quantitative aspects of the silica gel trapping system (Appendix B.2.) were so much improved over the condenser system, our emphasis has since been on evaluation of data collected using this exhaust collection system. The collection results of several samples from the three load conditions are given in Table 6.

The reproducibility in the total organics (TOE) collected at the 10 and 33% load conditions is good. However, the 90% TOE values vary considerably. The greatest amount of water is generated at the high load condition and we have noticed an inverse dependence on the TOE values and the amount of water collected on the silica gel. Efforts are currently in progress to minimize this effect. There is still a fair spread in the LCC-4 and LCC-10 values for any given load condition and studies are under way to determine the cause of this variation. Except for the obvious variation in TOE values, the effect of load on the fraction distribution

Table 6

Sample Distribution from Various Load Conditions
Silica Gel Trapped Exhaust

Sample Code	Load	TOE[a]	mg/Kℓ present in LCC Fraction[b] LCC-1	LCC-4	LCC-10
Gel 3	10%	230	160	4.2	9.2
Gel 4	10%	230	220	6.9	7.7
Gel 9	10%	300	126	10.8	10.3
Gel 5	33%	250	207	4.8	7.4
Gel 6	33%	240	219	15.6	7.3
Gel 10	33%	290	169	19.3	8.8
Gel 7	90%	50	32.3	3.7	11.5
Gel 8	90%	100	65.9	5.7	6.0
Gel 11	90%	150	82.1	11.1	8.6

a. Total Organic Extract before fractionation

b. LCC-1 = Paraffins, LCC-4 = Aromatics, LCC-10 = Oxygenates is not obvious from these data. The sources of variation in the data will first have to be understood before any clear correlations can be achieved.

The quantitative chemical class composition of each of the aromatic fractions was determined by the mass spectrometric computer analysis routine and the results are reported in Table 7. These data at the present time show sufficient variation within a load condition that any correlation of load and composition is precluded. However, the samples and data do provide a valuable interim means to evaluate the correlation between odor and composition of specific samples.

3. Odor of Exhaust Samples

The odor evaluations reported in Table 8 represent collections on silica gel at the 10, 33, and 90% load conditions obtained for comparison with early studies of condensate samples. The most significant finding is the obvious improvement in recovery of odorants, so that the total organic extracts are recognizable at slight to moderate intensities when examined in the test room at the equivalent of 20 liters.

When examining fractions from aqueous extracts, test levels equivalent to 200 liters of exhaust were normally used. In some instances these were increased to 400-liter equivalents to obtain definitive descriptions. It is also apparent from the relative intensities shown in Table 8 that the 33% load yields a relatively higher odorant recovery, possibly because this has been the standard process.

From the odor profile examination of the TOE from the gel trap at 33% load, there is still some loss evident in the TIA, in comparison with the total exhaust. Oxidized oil odor notes are detected in the same relative intensities as found in the total exhaust. Kerosene is just perceptible and is significantly lower, while some general irritation is evident.

LCC-4 exhibits very slight intensities of both kerosene and oily aromatics, which might be expected when compared with the TOE. LCC-10 indicates a slight loss of smoky burnt compounds. Both oxidized oil and smoky odor notes are detected at slight intensities, and eye and nose irritation are again noted.

At the 10% load, the characteristic sour oxidized oily aromatic is apparent in the TOE with a burnt, smoky secondary odor. No kerosene aromatics are detectable at 20-liter equivalent, which is consistent with the 33% load findings. In the examination of the LCC-4 fraction, kerosene per se is not identified, but a very slight level of a sweety solventy aroma and some pungency are noted. The oxygenated fraction (LCC-10) is dominated by a sour oxidized oil character and a smoky sooty odor both observed at intensities at least as high as found in the total extract. Eye and nose irritation are apparent as well.

Table 7

Aromatic Composition Analysis of Fractions from Various Engine Loads

	% Composition								
Engine Load, %	10			33			90		
Gel Sample	3	4	9	5	6	10	7	8	11
Chemical Class									
Alkyl Benzenes	46	43	47	49	42	44	52	44	42
Indans/Tetralins/Indenes	8	10	16	6	18	26	3	9	24
Naphthalenes	44	49	39	42	44	33	41	46	37
FOE	7			16			6		

Table 8

TEST ROOM ODOR EVALUATIONS OF SAMPLES FROM VARIABLE LOAD[a]

	Gel 4 - 10% Load		Gel 6 - 33% Load		Gel 8 - 90% Load	
Total Exhaust	TIA	2	TIA	2	TIA	1½-2
	Sour oxidized oil	1½-2	Smoky tarry	2	Burnt tarry	1½
	Burnt smoky (part.)	2	Oxidized oil	1½	Kerosene	½
	Kerosene	1	Kerosene	1-1½	Oily (metallic)	)(
	Nose irritation	✓	Nose irritation	✓		
	Eye irritation	✓	Eye irritation	✓		
Total Organic Extract (TOE)	TIA	1-1½	TIA	1½	TIA	1-1½
	Sour oxidized oil	1	Smoky burnt	1½	Smoky (sooty)	1-1½
	Burnt sooty	1	Oxidized oil	1-1½	Burnt	½
	Irritation	✓	Kerosene	)(	Oily metallic	½-1
			Irritation	✓	Irritation	✓
Aromatic LCC-4 Fraction	TIA	½	TIA	½-1	TIA	1
	Solventy sweet	½	Solventy kerosene	½-1	Oily	)(
	Oily	)(	Oily	½-1	Kerosene	?
	Pungent	✓			Caramel	½
Oxygenate LCC-10 Fraction	TIA	1½	TIA	1-1½	TIA	1
	Sour oxidized oil	1½	Oxidized oil	1	Smoky (sooty)	1
	Smoky (sooty)	1	Leathery	1	Oily	½
	Eye irritation	✓	Smoky	1	Irritation	✓
	Nose irritation	✓	Nose irritation	✓		
			Eye irritation	✓		

---

a. 20ℓ samples of exhaust or the equivalent of the analytical fractions.

At 90% load, the dominant odor note -- both in the exhaust and in the TOE -- is a heavy smoky character although at a noticeably lower intensity in the latter. The sharp oily metallic characteristic is also detectable at a very slight level in the total organic extract, but it was just perceptible in the total exhaust.

Kerosene was not detected in the TOE, and its presence was questionable in the LCC-4 fraction which exhibited little relation to diesel exhaust. The oxygenate fraction produced the lowest TIA of the set and exhibited the smoky, sooty odor observed in the total organic extract at a slight intensity. Some irritation was noted but less than the two comparable samples from 10 to 33% loads. This is consistent with the sensations observed in the original exhaust.

B. FUELS

1. Analytical and Odor Evaluation

We have compared the odor characteristics of three new diesel fuels of varying aromatic content to the No. 1 diesel fuel presently used as well as several aromatic-free paraffin mixtures. The alternative diesel fuels studied were:

East Coast Diesel No. 2

Heating Oil

Midwest Diesel No. 2

The Phillips Petroleum Company has available several aromatic free paraffin mixtures of narrow (Soltrol's) and wide (Base Oil's) boiling ranges. The Soltrol 170,200 and Base Oil No. 1 have properties similar to those of the diesel fuels and were also examined for odor characteristics. The Phillips paraffin mixtures have a considerably cost advantage for our testing program compared to similar quantities of heptane or cetane.

Some of the physical and chemical properties of these materials are given in Table 9. The aromatic portion of the diesel fuels was isolated in the LCC-4 fraction by the liquid chromatography method for odor study. The observed contribution of this fraction to the total sample mass determined by the GC method is also included in the table.

The detailed composition of the aromatic portion of these fuels was determined to provide a test of the odor character-composition correlation developed for the oily-kerosene odor complex and is reported in Table 10.

The fuels and LCC-4 fractions were examined in detail in the odor test room. None of the Phillips paraffins had any recognizable odor, and each would be acceptable for study as a paraffinic fuel. The boiling range data indicate the Soltrol 200 or Base Oil No. 1 would provide the best general diesel match. We had a preliminary preference for the Soltrol 200,

Table 9

Physical/Chemical Characteristics of Alternative Fuels

Fuels	Sp. Gr.	Distillation Range (°F)		Composition (%)				
		10-90%	50%	Aromatics[a]	Olefins[a]	S	Silica 4[b]	NMR[c]
No. 1 Diesel (Year 2)	0.832	396-497	436	20.8	2.8	0.19	11	13
East Coast Diesel No. 2	0.826	424-566	482	24.1	1.8	0.20	10	14
Midwest Diesel No. 2	0.852	418-586	506	34.7	2.2	0.29	18	23
East Coast Heating Oil	0.854	430-585	498	35.4	2.0	0.24	16	25
Soltrol 170		424-460	442					
Soltrol 200		460-495	478					
Base Oil No. 1		357-549	453					

a. volume %, FIA
b. weight %, FOE
c. mole %

Table 10

Aromatic Composition Analysis of Alternative High Aromatic Fuels

Compound Class	% Composition in No. 1 Diesel	East Coast No. 2 Diesel	Mid West No. 2 Diesel	East Coast Heating Oil
Alkyl benzenes	32	12	3	2
Indans/Tetralins/Indenes	38	13	6	4
Naphthalenes	32	52	61	70
Acenaphthenes, etc.		16	21	17
Phenanthrenes, etc.		7	10	6

since it is chemically simpler and would, therefore, somewhat simplify the analyses. One engine test was made with this fuel. In the course of the analyses, however, we found that the Soltrol 200 did have a small aromatic content. Future studies will be done with the base Oil No. 1 which was found to be free of aromatics.

The test room data for the high aromatics fuel samples is given in Table 11. Of the four samples, the Midwest diesel has the highest total intensity of aroma and the most complex odor at this concentration. It has both kerosene-type and tarry odors with an oxidized oily note at a slight to moderate intensity. It produces both eye and nose irritation and has some naphthenate-related odor. The heating oil is similar to this with a slightly lower total intensity of aroma and somewhat less complexity. At close to moderate intensity, the kerosene is the dominant identifhing odor and is somewhat lighter than that observed with the Midwest diesel. This character note is supported by an oxidized oily note which does not have linseed overtones. Naphthenate is present at a slight level and tarry-related odor notes are present, but just detectable as in the Midwest diesel fuel sample.

The existing No. 1 diesel fuel also has a moderate total intensity of aroma. Kerosene is the primary character note and this is supported by an oily linseed-related character at less than moderate intensity. There is a very low level of naphthenate but no tarry aroma in this sample. Both eye and nose irritation are evident.

The lowest total intensity of aroma is observed with East Coast Disel No. 2, which has an intensity of slight to moderate (1½) -- this is cominated by the kerosene odor and the associated oily linseed-type aroma. Musty naphthanate is also apparent in this sample at a slight intensity. Interestingly, although eye irritation is evident in the sample, nose irritation is not observed. Of the four fuel samples, then, this has the lowest intensity of odor and feeling sensation.

The LCC-4 fractions derived from each of the fuels correspond fiarly well with the odor character and description of the original samples. There is in general some slight reduction in total intensity of aroma in the samples as well as in the recognizable intensities of the character notes. This is particularly true in the Heating Oil fraction. Kerosene continues to be the dominant character note in the Midwest diesel fuel fraction. This is supported by a tarry, almost phenolic odor note. The tarry odor character may be associated with the acenaphthenes, etc. present in this sample and not experiences before in the studies with the No. 1 fuel. The oily note does not appear to be oxidized as in the total sample, which may indicate some presence of oxygenated components in the fuel. Musty naphthenate is present as are eye and nose irritation.

With the Heating Oil, the total intensity of aroma is reduced by a slight amount in the LCC-4 fraction as are the kerosene and oily odors. The naphthenate appears to be slightly tarry in character and is the character note of highest intensity in this sample, which correlates with the character observed in the Midwest diesel fuel. Both eye and nose irritation are apparent.

TABLE 11

Odor Test Room Evaluation of Fuels and Aromatics Fractions

Fuel	Odor[a]			
	Fuel		LCC-4 Fraction	
No. 1 Diesel (Year 2)	2		2	
	Kerosene	2	Oxidized oily sour	1½
	Oily painty	1½-2	Kerosene	1½
	Naphthanate	½-1	Tarry naphthanate	½-1
	Eye irritation	✓	Eye irritation	✓
	Nose irritation	✓	Nose irritation	✓
			Headache	✓
East Coast Diesel No. 2	1½		1½	
	Kerosene	1½	Kerosene	1½
	Oily painty	1½	Rubbery	1-1½
	Musty naphthanate	1	Tarry	½-1
	Eye irritation	✓	Oxidized oily	1
			Eye irritation	✓
East Coast Heating Oil	1½-2		1½	
	Kerosene	1½-2	Kerosene (solv)	1
	Oxidized oily	1-1½	Oily	1
	Naphthanate	1	Tarry naphthanate	1-1½
	Tarry	✓	Eye irritation	✓
	Eye irritation	✓	Nose irritation	✓
	Nose irritation	✓		
Midwest Diesel No. 2	2		2	
	Kerosene	2	Kerosene	1½-2
	Tarry	1½	Tarry phenolic	1½-2
	Oxidized oily	1½	Oily	1
	Naphthanate	1	Musty naphthante	½-1
	Solventy	½	Eye irritation	✓
	Eye irritation	✓	Nose irritation	✓
	Nose irritation	✓		

a. 150 µl injected into 12,600 ℓ test room.

The existing No. 1 fuel has a moderate total intensity of aroma in the LCC-4 fraction, but the oily character, which is slightly oxidized, appears as the first character note in the profile description. Kerosene is at a similar intensity but appears as the second character note suggesting a slightly lower importance of this characteristic. There is a slight level of naphthenate or tarry-naphthenate and both eye and nose irritation are observed. The headache effect was also observed in this sample.

The East Coast Diesel No. 2 fuel is the lowest in total intensity of aroma and is the only sample in which we observe a new character note in the LCC-4 fraction. Kerosene is the dominant aroma, and there is a character note described as rubbery which was not observed in the total sample. It is recognized at a slight intensity in the LCC-4 fraction. Tarry or naphthenate is detected at a very low level and oxidized oily is present at a slight intensity. Again, eye irritation is the only irritation factor noted in this sample.

Of primary importance in this examination is the apparent demonstration of reasonable recovery of the identifhing odor characteristics in the LCC-4 fraction and the correlation in odor character as well as the general correlation in odor intensity of these fractions with the total fuel sample. It is interesting to note that, in some preliminary experiments, the solventy kerosene odor can be recognized with 1.5 μℓ of sample in the test room representing a 1/100 dilution of the normal test room concentration.

2. Engine Study of Soltrol 200

An initial study of the exhaust odor and analytical characteristics of Soltrol 200 was carried out to study the characteristics of an aromatic free fuel. In the course of the study we found that the fuel did indeed have a small aromatic content and future studies will be carried out with the aromatic free Base Oil No. 1.

The results obtained from this study are summarized in Table 12. The fuel consumption rate is close to that observed with the No. 1 reference diesel fuel. The amount of organic material collected from the exhaust is slightly higher than that observed for the diesel fuel (390 mg/Kℓ vs. 260). The liquid chromatographic fractionation shows that the aromatic content of the exhaust sample is the same as the original fuel. The composition analysis of the aromatic fractions is also approximately the same suggesting that all of the aromatics came from the fuel. Further studies of a completely aromatic free fuel will resolve any remaining questions about the synthesis of aromatics in the combustion process. It is interesting that the oxygenate content of the exhaust sample is the same percentage as the aromatic content and may just be a coincidence which does not have any direct bearing on the aromatic content.

The odor of the Soltrol exhaust is quite different than that of the diesel fuel exhaust being lower in total odor intensity (TIA 1½ vs. 2-2½) and totally different in character. The kerosene odor note is completely absent, as expected, based on the sample analysis. The exhaust odor is

Table 12

Summary of Soltrol 200 Engine[a] Test Results

Fuel Consumption: 8.8 Kg/hr (vs. 8.2 average for No. 1 Diesel)

Silica Gel (Gel 16) Total Organic Extract: 390 mg/Kℓ

Liquid Chromatographic Analysis:

LCC Fraction	Soltrol Fuel	Gel 16 Exhaust
SiO_2-1	98%	96%
-4	1.3%	1.5%
-10	0.0%	1.6%

Aromatic Composition Analysis

Chemical Class	Soltrol Fuel	Aromatic Exhaust Fraction
Alkyl benzenes	48%	56%
Indans/tetralins/indenes	30%	21%
Naphthalenes	16%	21%

Odor Characterization (20 ℓ)

Exhaust	Total Organic Extract	Oxygenates Gel 16 LCC-10
TIA 1½	TIA 1-1½	TIA 1½
Smoky candle 1-1½	Smoky candle 1½	Smoky candle 1½
Sour oxidized 1	Sour oxidized ½-1	Sour oxidized ½-1
Irritation √√	Irritation √	irritation √√

No odor observed in LCC-4 aromatic fractions

a. 33% load

characterized by a moderate intensity of smoky candle and sour oxidized and a strong irritation factor. This same odor character is also found in the total organic extract and seen to be due entirely to the oxygenate fraction which has essentially the same odor as the original exhaust.

We expect that the observed odor character can be accounted for primarily in terms of alkenone and furan (R+DB 2 and 3) type species. The sample will be analyzed in detail once the oxygenate analysis scheme (Section IV D.2.) is completed.

VI. ODOR/CHEMICAL ANALYSIS CORRELATION

Our attempts to establish a quantitative odor/composition correlation are still in the very preliminary stages. However, several observations have been quite encouraging in this regard. Sufficient odor and quantitative composition data have been obtained from the engine load studies using the No. 1 diesel fuel to explore the correlation between the oily and kerosene odors in the LCC-4 aromatic exhaust fractions and the amount of alkyl benzenes and indans/tetralins present in the samples.

From the composition analysis data we were able to calculate the amount of each of these chemical classes present in the test room when the odor of the LCC-4 fraction was determined. These data can then be compared with the sample odor intensity as shown in Table 13. The data have been obtained from our studies on exhaust collected by both the condenser and silica gel systems and represent a wide range of concentration of samples studied.

Although there is not yet a great deal of resolution or accuracy on either the composition or odor scales, it is apparent that the samples with the highest concentration of indans/tetralins have the highest kerosene odor intensity -- while those with the lowest concentration correspondingly have the lowest odor intensity. The two samples with intermediate concentrations of these species are not differentiated on the limited odor intensity scale. It is important to remember at this point that there is a logarithmic relationship between sample concentration and odor intensity so that minor differences in sample concentration will tend to be unresolved on the odor intensity scale.

The first and last two sets of results for the alkyl benzenes show the same relationship to the oily odor intensity, but the one intermediate observation does not fit the trend.

Overall, these first attempts at establishing a correlation between composition and odor have been quite encouraging and suggest that we are proceeding in the proper direction. The most appropriate point is that our data analysis schemes provide maximum flexibility in shifting the direction of our correlation emphasis without requiring any fundamental change in the data acquisition steps.

Table 13

Comparison of Oily-Kerosene Composition and Odor Intensity[a]

Sample	Kerosene		Oily	
	µg of Indanes/Tetralins	Odor Intensity	µg of Alkylbenzenes	Odor Intensity
Gel 4[b]	14	½	60	)(
Gel 8[b]	12	½	50	)(
Gel 6[b]	54	$\underline{\underline{\frac{1}{2}}}$-1	120	½-1
Cond 66[c]	68	½	70	-
Cond 67[d]	160	½-$\underline{\underline{1}}$	170	½
Cond 65[c]	300	½-$\underline{\underline{1}}$	520	½

a. LCC-4 fractions studied in odor test room

b. 20ℓ sample
c. 200ℓ sample
d. 400ℓ sample

VII. REFERENCES

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VIII. GLOSSARY

The following terms have been used frequently in the text and are summarized here with their definitions, for the convenience of the reader.

Cond. - Abbreviation for condensate representing the sample collection used resulting in an aqueous condensate from the diesel exhaust.

GC - Gas Chromatography, used for sample comparison and quantitative measurement.

Gel - Sample code name for exhaust samples collected using the silica gel method.

FOE - Fuel Oil Equivalent, the quantity of exhaust species present in a sample as measured by the flame ionization detector response when compared to the response calibration with fuel oil.

HRMS - High Resolution Mass Spectrometry, used for chemical identification, and quantitative mixture analysis of the oxygenate fraction.

LCC - Liquid Column Chromatography, used as the means of separating the paraffin, aromatic, and oxygenate fractions of the organic extract from the exhaust condensate. The procedure results in a series of fractions LCC-1, LCC-2, etc. Fractions LCC-4 and LCC-10 contain the aromatic and oxygenate exhaust odor complexes.

TIA - Total Intensity of Aroma, see Appendix A for details.

TOE - Total Organic Extract, the total organic exhaust species isolated from the sample collection by solvent extraction.

R+DB - Rings plus Double Bonds, a representation of chemical structure type by expressing the degree of hydrogen unsaturation (see Appendix E).

APPENDIX A

ODOR PROFILE TECHNIQUE*

1. SUMMARY

The standard diesel exhaust sample has been defined as a 2½-min. post-muffler exhaust aliquot of 21ℓ taken during normal engine operation and a 25 kw (33%) load after warm-up. The profile analysis of the standard sample diesel exhaust was consistent from day to day, but the odor of diesel exhaust did show some differences with variations in engine operation. Preliminary studies indicate that within the normal procedural time interval between sampling and examination, there are no detectable losses. Indeed, the odor appears to persist with only slight change for over one hour. Total profile characterization is consistent with the odor observed when traveling behind a bus, which confirms our belief that the mode of engine operation provided a representative sample for analytical studies.

The description of the diesel exhaust odor in the test room with a dilution ratio of 600:1 can be described by three character notes: oily, represented by technical grade hexadecane among other standards; burnt, which, although similar to a low dilution of propionaldehyde, phenol, and cresol, is produced in fuels with partial oxidation at elevated temperatures, and kerosene, which is the top odorous component of the fuel and may be described as having sweet, sharp, sour, tarry, and solvent components. In addition to these odor characteristics which appeared in the slight-to-moderate intensity range at this dilution, two feeling sensations - nose irritation and eye irritation - were apparent.

As implied by the descriptive terminology used, some of the odor characteristics are present in the fuel itself. The odor characterization of a 150μℓ aliquot of fuel, which (by computation) is equivalent to the amount of fuel burnt to produce the 21-ℓ sample of exhaust, produces an odor in the test room at least as strong as the exhaust odor. The dominant odor characteristic is kerosene, with the oily note being less intense and the burnt aroma barely detectable. With the diesel exhaust, the oily and burnt aromas are primary character notes and kerosene a supplementary factor.

2. ODOR PROFILE METHODOLOGY

The odor Profile Method of analysis has proven useful in flavor and odor studies in a wide range of food and nonfood products. The Profile Method, which originated at Arthur D. Little, Inc., 25 years ago, is a semiquantitative and qualitative description of the odor sensation. The total odor sensation can be described by six character notes. The method is qualitative in that there is verbal description as to the odor quality(s) perceived. The order of appearance of odor character notes indicates the other odor qualities present as a function of time on a microsecond basis.

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* Taken from Final report of first year's work, July 1969, "Chemical Identification of the Odor Components in Diesel Engine Exhaust."

The intensity of each character note (as well as the Total Intensity of Aroma, TIA) is rated on a four-point scale ranging from threshold-)(, slight-1, moderate-2, to strong-3 intensities. It has been our experience that for the odor intensity to increase by one unit (i.e., from slight to moderate), a ten-fold increase in concentration is required. The threshold intensity indicates that the character note detected is just recognizable. The basic four point scale of threshold-)(to strong-3 intensity can be expanded into a seven point scale with experienced panelists by the use of one-half ratings. Thus, the full scale of intensity rating of the odor strength is summarized below.

Numerical Rating	Intensity
)(	Threshold (recognition)
½	Very Slight
1	Slight
1½	Slight to Moderate
2	Moderate
2½	Moderate to Strong
3	Strong

The presence of feeling sensations is indicated by a check mark (✓) without any effort to describe their intensity. Four trained analysts form the odor profile panel. The sample to be analyzed is presented to the panelists in a standard manner. In this study, each of the four panelists entered the odorized test chamber independently of one another and sniffed the air three times. Each then recorded his observations on the odor character notes perceived, their order of appearance, and their intensity. After the observations in the test room, the panalists gathered to discuss their results. Reference was made to odor standards to relate the various verbal descriptions used and to develop common language in describing the odor quality. Reference odor standards may be single chemical species or may refer to a mixture of chemicals.

The panel's results were then composited into an odor profile that summarized the odor observations of the four panelists and indicated the odor quality, the order of appearance of the characteristic notes and their intensities.

3. ODOR TEST ROOM

The Odor Test Room consisted of an antechamber, an odor chamber, and supporting equipment such as fans, ducts, activated carbon, air intake, and air exhaust motors. The air is treated with activated carbon (C-42 cannister from Dorex) and provided a low-odor background diluting medium and was also used to flush odorized air from the chamber and acclimate the four panel members to a low odor background. The odor chamber where the odor studies were carried out was an aluminum-clad room with a volume of 12,600ℓ. Previous studies have shown polished aluminum to be satisfactory for odor studies because it has a low odor background. Fans in both the odor chamber and antechamber ensured adequate mixing and assisted in flushing the test room with odor-free air.

The sequence of events occurring prior to an odor observation by the panel in the test room is listed below.

a. Odor-free air is used to flush out the antechamber and odor chamber.

b. The door connecting the odor chamber and antechamber is closed thus sealing the odor chamber.

c. Diesel exhaust is injected into the odor chamber through a sampling line by means of a swivel-jointed sampling system. Three fans located in the odor chamber circulate the diesel exhaust with the diluting air to ensure proper mixing. Five minutes after injection the fans are shut down, and the odorized air in the odor chamber is allowed to come to rest.

d. The four panel members then enter the antechamber where they become acclimated to the low odor background air.

e. The panel then enters the odor chamber, one at a time, to make observations.

f. The cycle is then repeated to prepare the odor test room for the next observation. A 20-minute flushing period has been found to be adequate for removing odor from the test room.

4. ODOR ANALYSIS - DIESEL TEST SAMPLES

Reference odor profiles on diesel exhaust itself have been developed using a 21-ℓ injection of exhaust into the odor test room (600/1 dilution). Because the condensation sample collection procedure collects only about 10% of the odor in the condensate, it is necessary to inject 210-ℓ aliquots of the extracted fractions into the test room for their odor evaluation.

APPENDIX B

DIESEL EXHAUST SAMPLING SYSTEMS

1. HIGH VOLUME EXHAUST SAMPLING SYSTEM

A trapping system capable of accumulating large volumes of diesel exhaust over a shorter period of time was constructed to aid our studies in several areas. The small amount of organic material isolated in the chloroform smoky-burnt fraction required 20,000 - 30,000 liters of exhaust aliquot for a single GC-MS experiment. Therefore, the trapping system was redesigned so that we could more efficiently trap the amounts of sample required for the identification phase of the program. The high sampling rate also enabled us to more efficiently study the engine and fuel variables and simplified the evaluation of the quantitative analytical methods.

With our original trapping system, we were only able to collect about 1000 liters per hour, and the accumulation of 50,000 liters of exhaust condensate entailed the inconvenience of maintaining the system in continuous operation for at least 48 hours. Thus, we have modified our trapping system to effect a ten-fold increase in collection capacity, i.e., volume throughputs of about 10,000 liters per hour. This increase was accomplished by a general scale-up of our original system without incorporating any basically new, and therefore unknown, approaches. The new system is shown schematically in Figure B-1.

The exhaust gas is channeled into two streams which can be filtered simultaneously through the large, heated, double filter. The dual filter holder is a section of 12" diameter x 3" stainless steel tubing which has been fitted with two sets of stainless screens slightly inset to support the 11-inch glass fiber sheets. The sheets also act as gaskets between the main body and the headers. Each header is fitted with three flat heaters (600 watts per side) to maintain the filter at the exhaust gas temperature.

The flow of filtered exhaust gases is directed down through a 1-inch opening into a QVF Model HE-4 glass condenser heat exchanger containing 5 square feet of heat exchanger surface. The exhaust condensate is collected in a cooled 5-liter, one-necked flask situated immediately below the condenser and connected to it by a tee. The residual exhaust gases are drawn through the dry gas meter by the carbon vane pump and vented to the atmosphere. Pressure drop through the system is measured by a manometer just downstream of the meter to allow for pressure corrections if necessary. The temperature of the condenser and flask is maintained at 0°C by circulating coolant from a reservoir which is chilled by a 1.5 hp compressor.

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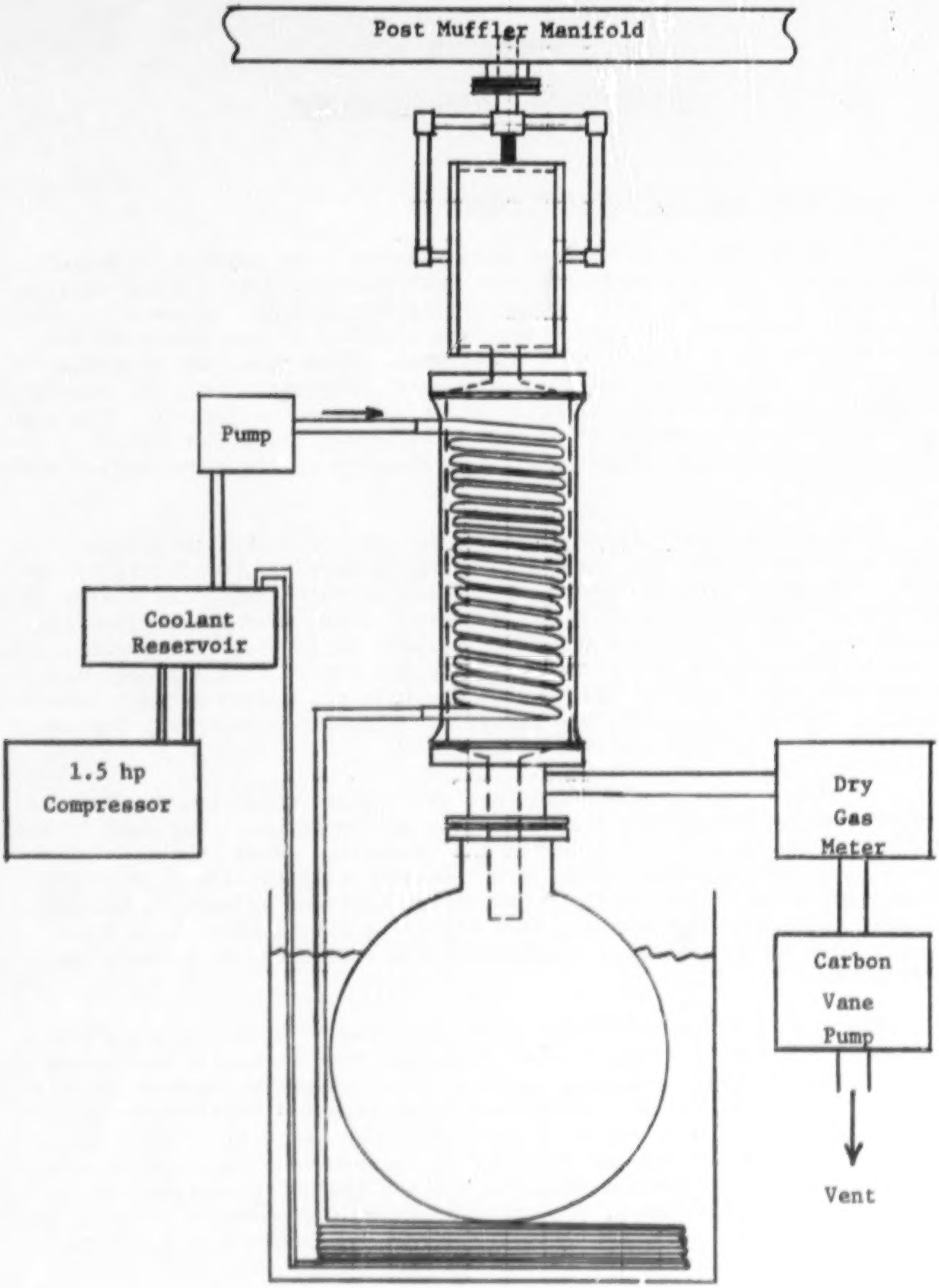

Figure B-1 - High Volume Diesel Exhaust Sampling System

2. SILICA GEL COLLECTION METHOD

Exhaust is sampled from the exhaust manifold by means of a heated particulate filter and heated lines to and from a teflon diaphragm Dynapump which provides a 0.5 cfm sampling rate. The exhaust sample is passed from the pump through a tube (approximately 2 cm dia. x 10 cm long) containing 25 g of silica gel (Fisher Scientific, 14-20 mesh) which has been acid washed (pH 1-2) and activated at 110°C. A slight odor and hydrocarbon breakthrough is noted after the collection of 720 ℓ in one hour. A distinct yellow-brown color is observed at the top of the gel trap where the silica is first contacted with the exhaust.

The absorbed sample is extracted from the gel by treating the silica in the collection tubes successively with 50 ml of pentane and 50 ml of 10% $MeOH/H_2O$ solution which is 0.01N in H_2SO_4. The aqueous acid methanol extract is re-extracted twice with 5 ml aliquots of $CHCl_3$. Analysis of the pentane and chloroform extracts suggests that 90% of the organic sample collected is extracted by the pentane. This extract consists primarily of the hydrocarbons. The aqueous acid methanol, on the other hand, is required to complete the extraction of the oxygenated species.

It should also be noted that the greater bulk of the sample collected on the gel trap consists of condensed water vapor and that the amount of organic sample collected bears an inverse relation to the amount of water trapped. No attempt has been made in the course of the present experimentation to control the water accumulation.

APPENDIX C

LIQUID COLUMN CHROMATOGRAPHY (LCC) PROCEDURES

1. STANDARD PROCEDURE*

In the standard first-stage separation technique, the sample is subjected to silica liquid-column chromatography. The detailed experimental conditions are as follows using the 76,500 liters of exhaust collected in Experiment 25 as an example:

> Column Conditions. 1.8 cm ID packed for a length of 20 cm with silica, Grade 950 (Fisher Scientific, 60 to 200 mesh) activated at 110°C for two hours.
>
> Sample Preparation. A small volume (15 ml) or organic condensate extract was mixed with 15 ml silica and transferred to the top of the column.
>
> Elution Scheme. Refer to Table C-1.
>
> Handling of Various Fractions. All fractions were allowed to evaporate overnight at room temperature and the final volume was adjusted to 7.65 ml in each case. Thus, for these examples representative of 76,500ℓ of exhaust.

The fractionation of the sample, along with the elution scheme and qualitative odor is given in Table B-1. Oily kerosene comes out in fractions 4 or 5 and the smoky-burnt odor character comes out in fraction 10. Since the total Sample 25 had a fuel oil equivalent (FOE) of about 5,000 mg.** about 70% of the mass was in fraction 1, 14% in fraction 5, and only 3% in fraction 10. This procedure was used in preparing the fraction for the identification phase of the smoky-burnt odor studies.

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*Taken from Final report of first year's study, ref. 1.

**Mass of sample as determined from flame ionization detector response based on calibration with fuel oil.

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TABLE C-1

SILICA LCC ELUTION SCHEME AND ODOR OBSERVATIONS FOR SAMPLE 25

Fraction	Solvent	Comment	FOE (mg) [a]	Odor [b]
1	Pentane, 150 ml [c]	Colorless effluent	3, 500	Odorless
2	Pentane, 100 ml	Colorless effluent		
3	Pentane, 100 ml	Colorless effluent		
4	Benzene, 100 ml	The yellow component starts moving down upon addition of benzene; collected effluent was still colorless		
5	Benzene, 100 ml	Greenish yellow effluent . . .	700	Oily, kerosene
6	Benzene, 100 ml	Greenish yellow		
7	$CHCl_3$, 150 ml	Light greenish yellow		
8	5%MeOH/$CHCl_3$, 100 ml	Very light greenish yellow		
9	10% MeOH/$CHCl_3$, 100 ml	Very light greenish yellow		
10	25% MeOH/$CHCl_3$, 100 ml	Brown	150	Smoky-burnt, oily
11	50% MeOH/$CHCl_3$, 100 ml	Brownish yellow		
12	MeOH, 125 ml	Yellow		

a – Fuel oil equivalent; weight of sample based on GC response compared to fuel oil calibration using the FID response from silicone column. Total FOE for Sample 25 =5000 mg.

b – Qualitative odor screening observation.

c – The eluted fractions were concentrated to 7.65 ml.

2. GRADIENT ELUTION PROCEDURE

The gradient elution procedure was used for the isolation of the smoky-burnt odor species from the separate pentane and chloroform extracts of the exhaust condensate. This procedure was found to give a resolved fraction having an improved odor/mass ratio, and resolution compatible with the two-stage GC-HRMS analysis procedure.

Column Conditions: 0.7 cm I.D. packed for a length of 14 cm with silica, Grade 950 activated at 110°C for two hours.

Sample Preparation: A small volume (5-10ml) of chloroform or pentane condensate extract was mixed with 2ml of silica and transferred to the top of the column.

Elution Scheme: Refer to Table C-2.

Fraction Handling: All fractions were allowed to evaporate until they had reached an equivalent concentration of approximately 10ℓ of exhaust/μℓ.

The elution sequence and order of odor elution is given in Table C-2. The effectiveness of the procedure for improving the smoky-burnt fraction can be seen in a comparison of fraction 38 from this example with a comparative smoky-burnt fraction obtained on the same initial sample using the standard procedure. While both the standard and modified odor fractions had a TIA of 1 and smoky-burnt odor intensity of 1, the standard fraction contained 0.6μg/1000ℓ compared to 0.04μg/1000ℓ for the gradient fraction.

3. MICRO COLUMN PROCEDURE FOR QUANTITATIVE ANALYSIS

A new micro LCC procedure was developed to simplify the analysis and meet the sample handling requirements of the 1000ℓ exhaust samples collected on the silica gel traps.

The concentrated pentane and chloroform silica gel extracts are fractionated in a micro-column, which consists of a bottom tapered 16 cm piece of 8 mm glass tubing fused to a 6 cm piece of 18 mm glass tubing which serves as solvent reservoir. The column is packed with activated silica Grade 950 (Fisher Scientific, 60-200 mesh) to a height of 12 cm. The volumes of the solvents used for eluting were adjusted correspondingly to establish chromatographic conditions similar to those of our standard LCC fractionation. The elution pattern and odor characteristics are shown in Table C-3.

TABLE C-2

GRADIENT ELUTION FRACTIONATION OF SAMPLE 43-$CHCL_3$ EXTRACT (3,000ℓ)(4)

Fraction No.	Solvent	Odor Notes[3]
1 to 6	Pentane, 5 ml	
7	5% $CHCl_3$, (1), 5 ml	Kerosene
8	5% $CHCl_3$, 5 ml	
9 to 12	10% $CHCl_3$, 5 ml	
13 and 14	20% $CHCl_3$, 5 ml	
15	20% $CHCl_3$, 7 ml	
16	30% $CHCl_3$, 5 ml	
17	30% $CHCl_3$, 5 ml	
18	30% $CHCl_3$, 5 ml	
19 to 28	30% $CHCl_3$, 5 ml	
29	30% $CHCl_3$, 5 ml	
30 to 31	35% $CHCl_3$, 5 ml	
32	35% $CHCl_3$, 5 ml	
33	40% $CHCl_3$, 7 ml	Oxidized oil
34 and 35	40% $CHCl_3$, 5 ml	
36	40% $CHCl_3$, 5 ml	
37	40% $CHCl_3$, 1 ml	Smoky-Burnt
38	40% $CHCl_3$, 2.5 ml	Smoky-Burnt
39	50% $CHCl_3$, 2.0 ml	
40 to 42	50% $CHCl_3$, 5 ml	
43	50% $CHCl_3$, 5 ml	
44	50% $CHCl_3$, 5 ml	
45	75% $CHCl_3$, 5 ml	
46 to 48	75% $CHCl_3$, 5 ml	
49 and 50	$CHCl_3$, 5 ml	
51	5% MeOH(2), 5 ml	
52	5% MeOH, 5 ml	
53	10% MeOH, 5 ml	Sour

1. % $CHCl_3$ in pentane
2. % MeOH in $CHCl_3$
3. Blotter Strip
4. Taken from final report, second year, ref. 2.

Table C-3

Micro-LCC[a] Fractionation of Gel Trap Samples[b]

Fraction No.	Solvent	Compound Type Eluted and Odor
1	Pentane, 10.0 ml	Aliphatic hydrocarbons; odorless
2	Pentane, 2.5	
3	Pentane, 2.5	
4	Benzene, 11.0	Aromatic hydrocarbons; oily kerosene
5	Benzene, 2.5	
6	Benzene, 2.5	
7	$CHCl_3$, 5.0	
8	10% MeOH/$CHCl_3$, 2.5	
9	10% MeOH/$CHCl_3$, 2.5	
10	10% MeOH/$CHCl_3$, 2.0	Oxygenated compounds; smoky burnt

(a) The micro-column used consists of a short glass tubing of 0.6 cm I.D. and packed with activated silica Grade 950 (Fisher Scientific, 60-200 mesh) to a height of 12.0 cm. The column volume is approximately 2.2 ml.

(b) The pentane and chloroform extracts of the gel traps were concentrated to about 1.0 ml and then applied directly to the top of the column.

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APPENDIX D

SILICONE AND CARBOWAX CHROMATOGRAMS OF SMOKY-BURNT FRACTIONS

The silicone chromatograms and odor profiles of the working samples are shown in Figures D-1 to D-3. All chromatograms were run at a temperature program of 4°C per minute from 70°C to 300°C. Samples 52C-34/5/6/ plus 56C-39/40 and Sample 56P-40 were analyzed on the same 10' x 1/8", 10% OV-1 column (D2 and D3) while Sample 51C-34/5 was examined on a similar but older column. Use of the two columns accounts for the difference in elution temperatures of the otherwise similar peak patterns shown in Figure D-1 as compared to the earlier elution temperatures observed in Figures D-2 and D-3. The silicone chromatogram of sample 60C was identical to that of samples 52C and 56C (Figure D-2) and has not been duplicated here. We have assigned peak numbers to similar peaks in each of the chromatograms as a constant working reference.

From Sample 51C-34/5 and Sample 52C-34/5/6 and 56C-39/40, we have trapped at the designated intervals over the region from peak 7 to peak 17. Peaks 18, 19, 20 and 21, 22, were trapped from Sample 60C. From Sample 56P-40, we have trapped from peak 10 to peak 22. The regions trapped are designated in the figures with broken lines. In our trapping experiments, we have tried to cover the reasonably intense peaks which are the significant odor contributors. Each trapped silicone peak was re-chromatographed on a 10' x 1/8", 5% SP-1000 Carbowax column, run under the temperature program designated in each chromatogram. (Figures D-4 to D-19). Odor profiles and high resolution mass spectra were obtained on each chromatogram. As described in the main text, the odor profiles and HRMS were obtained on separate trapped fractions with Sample 51, while the odor, GC response, and HRMS were all obtained simultaneously with Samples 52, 56, and 60.

The species or areas selected for HRMS examination on the basis of their odor are designated on the Carbowax curves by a code (2.0, 3.5, 9.0, etc.) which corresponds to the mass spectrometer photoplate exposure number.

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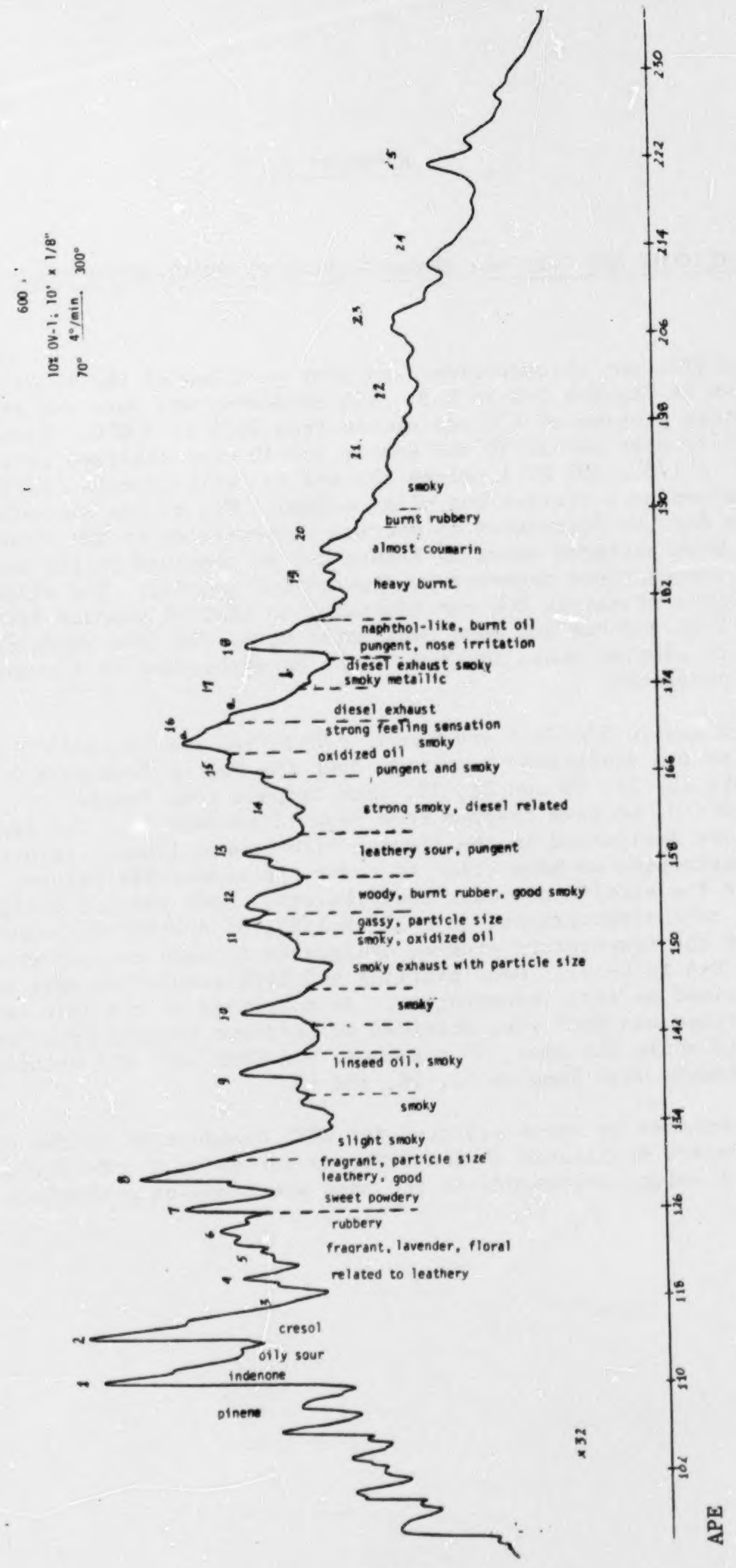

Figure D-1 SILICONE CHROMATOGRAM AND ODOR PROFILE OF SAMPLE 51C-34/5

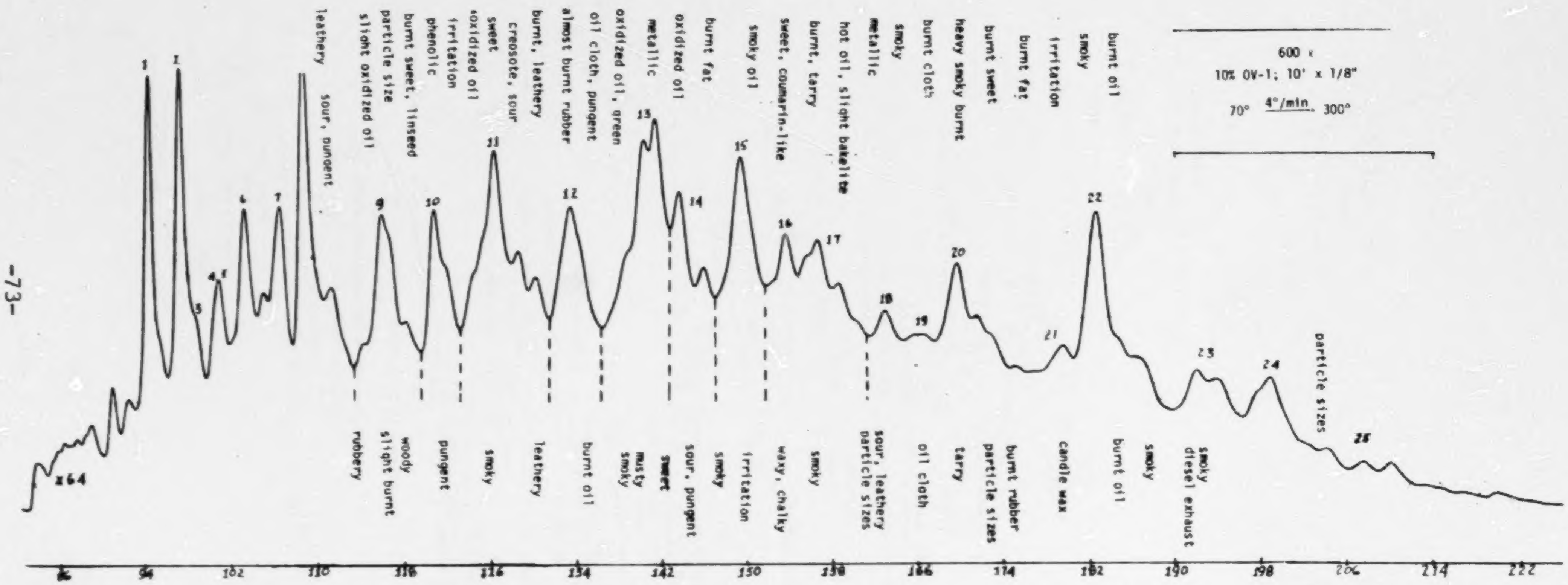

Figure D-2 SILICONE CHROMATOGRAM OF SAMPLE 52C-34/5/6 PLUS 56C-39/40

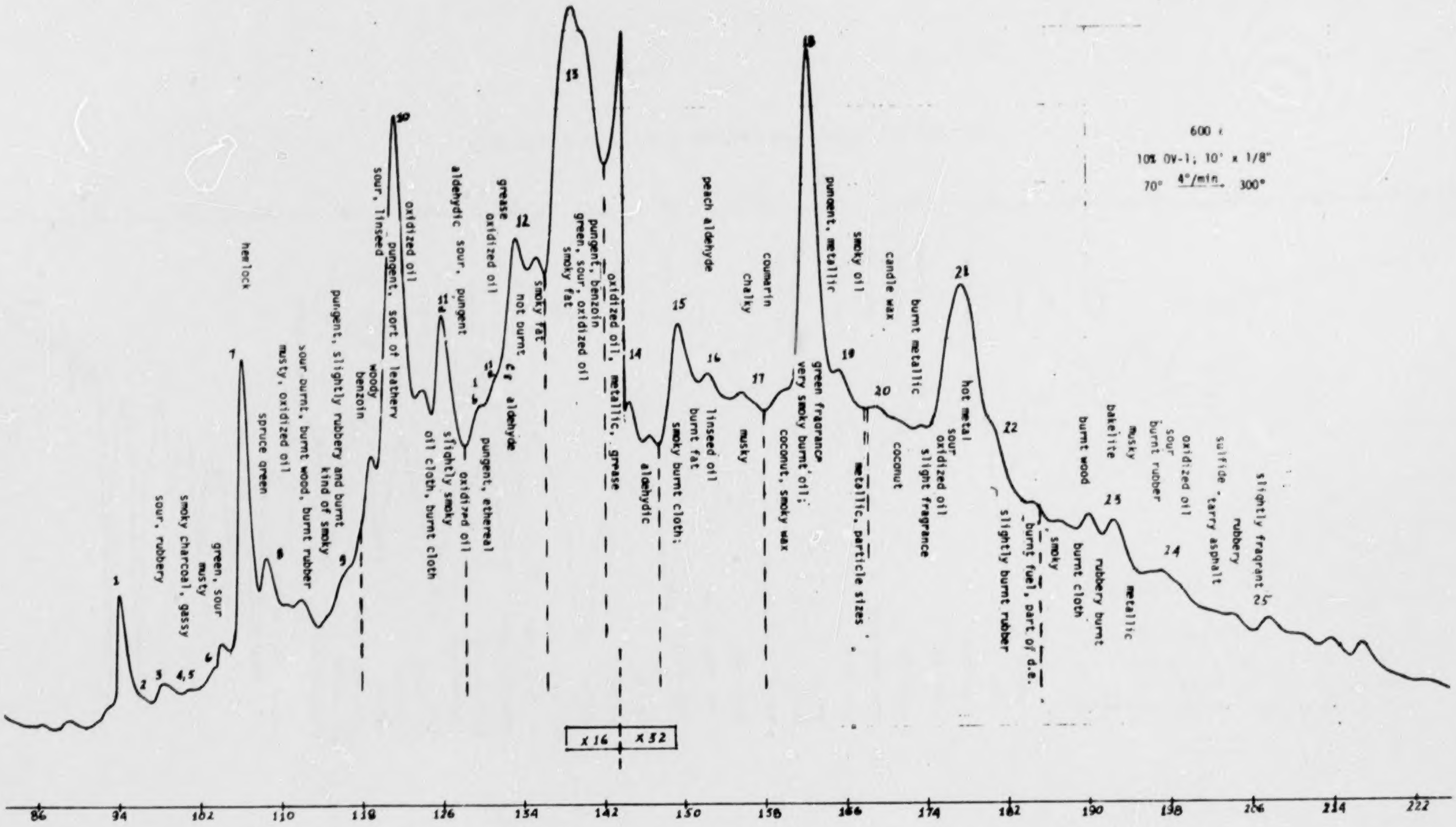

Figure D-3 SILICONE CHROMATOGRAM OF SAMPLE 56P-40

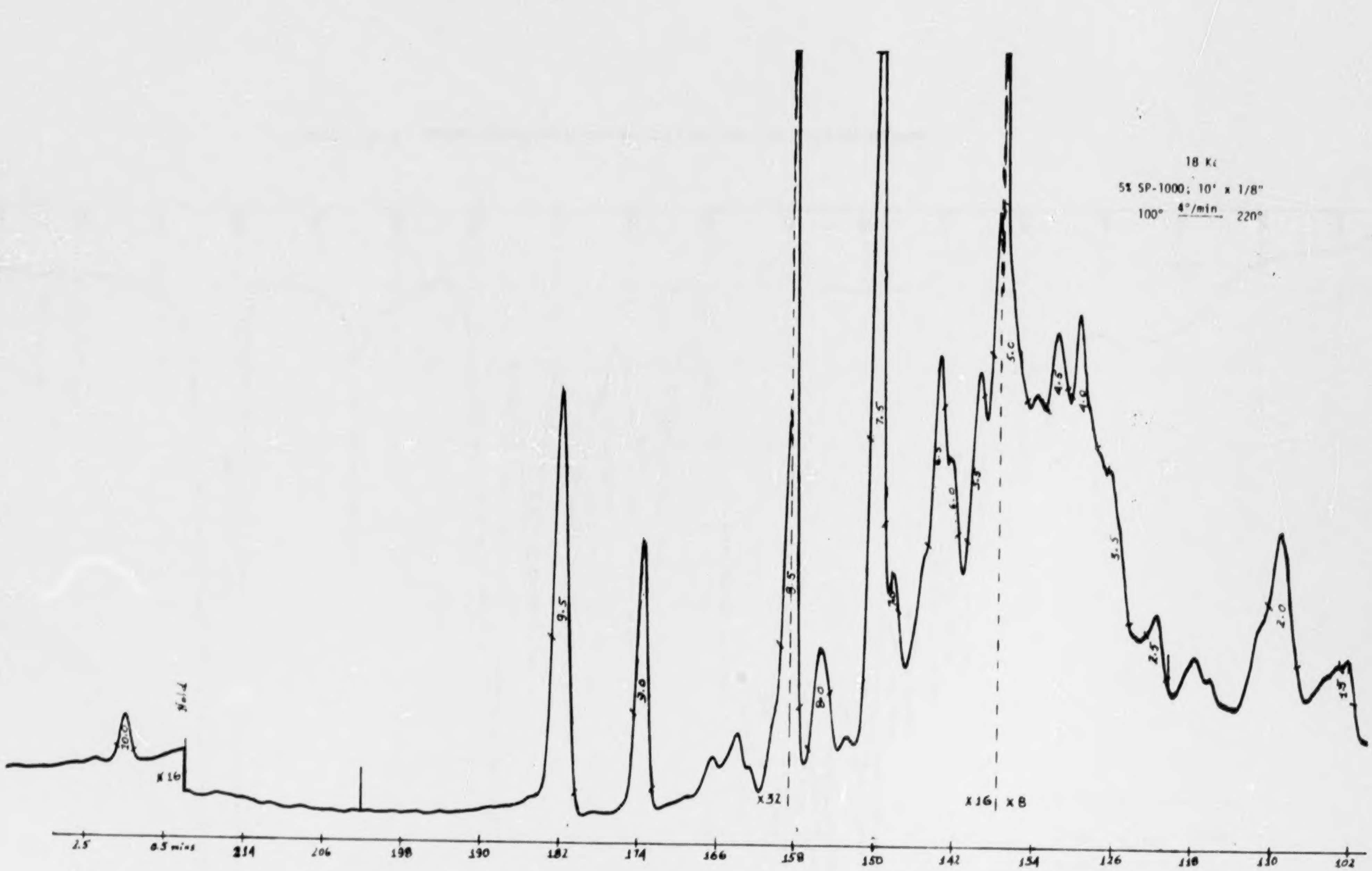

Figure D-4 CARBOWAX CHROMATOGRAM OF SILICONE PEAKS 7 AND 8 FROM SAMPLE SIC-34/5

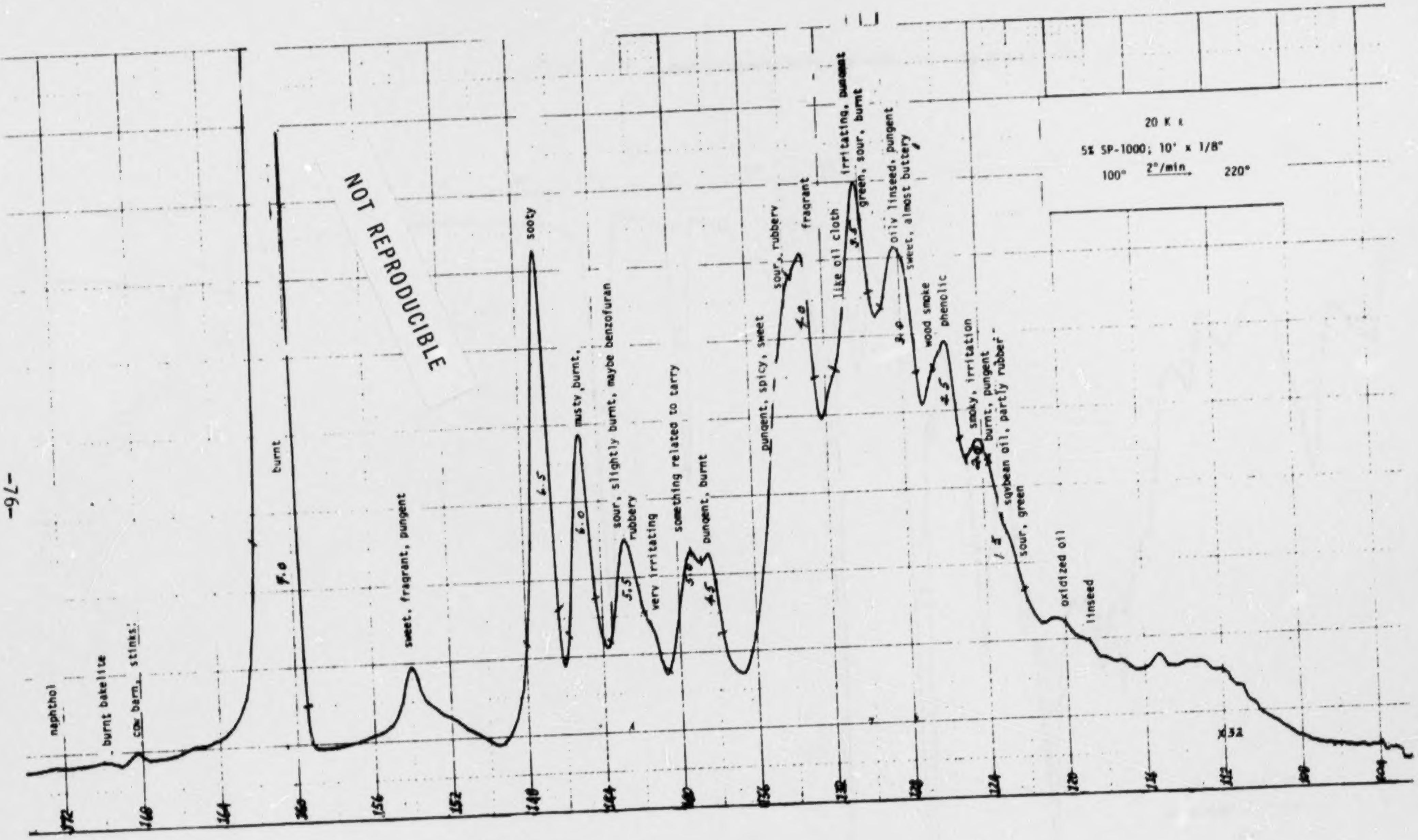

Figure D-5 CARBOWAX CHROMATOGRAM OF SILICONE PEAK 9 FROM SAMPLE 52C-34/5/6 AND 56C-39/40

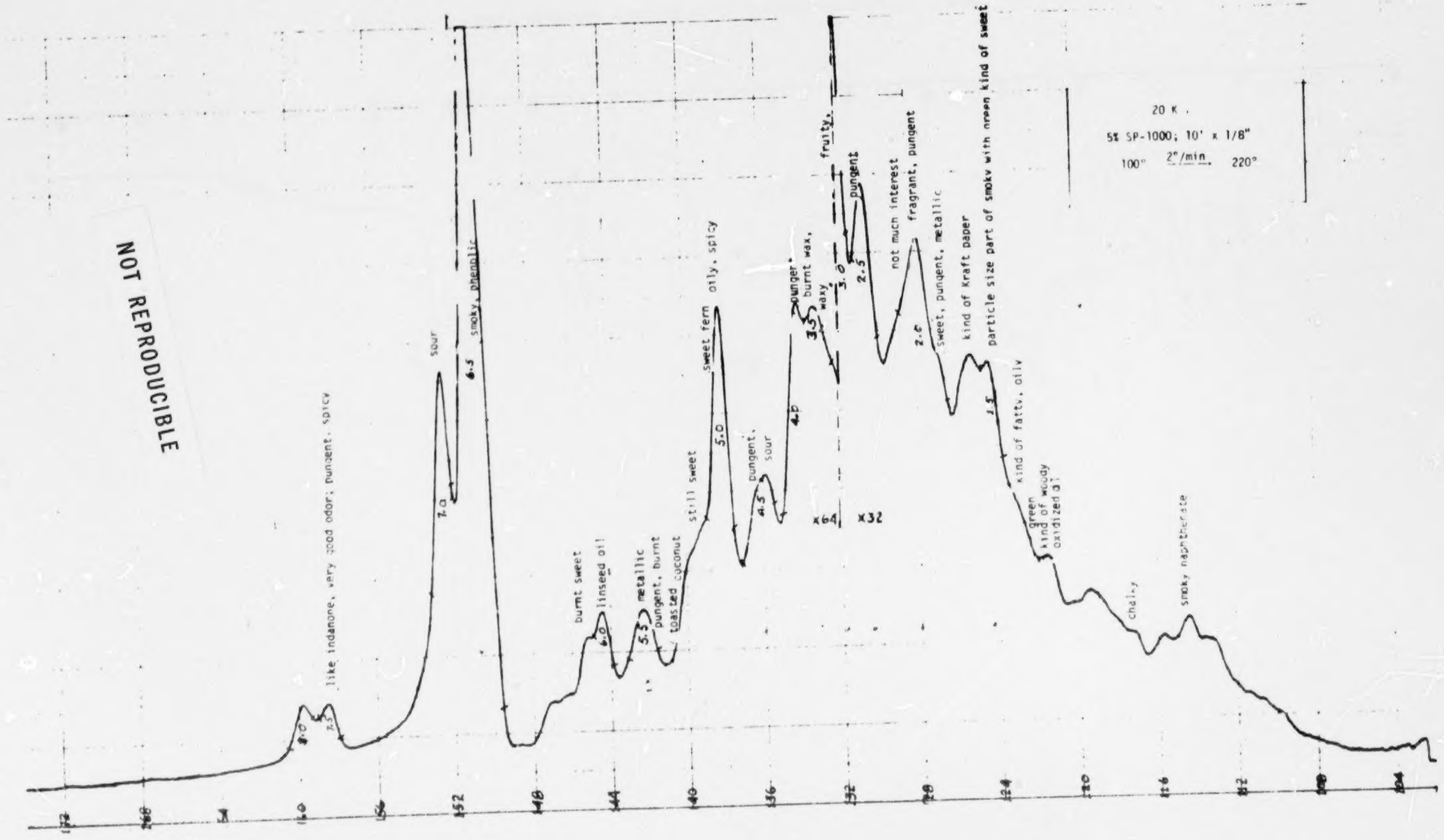

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Figure D-6 Carbowax Chromatogram of Silicone Peak 10 from Sample 52C-34/5/6 and 56C-39/40

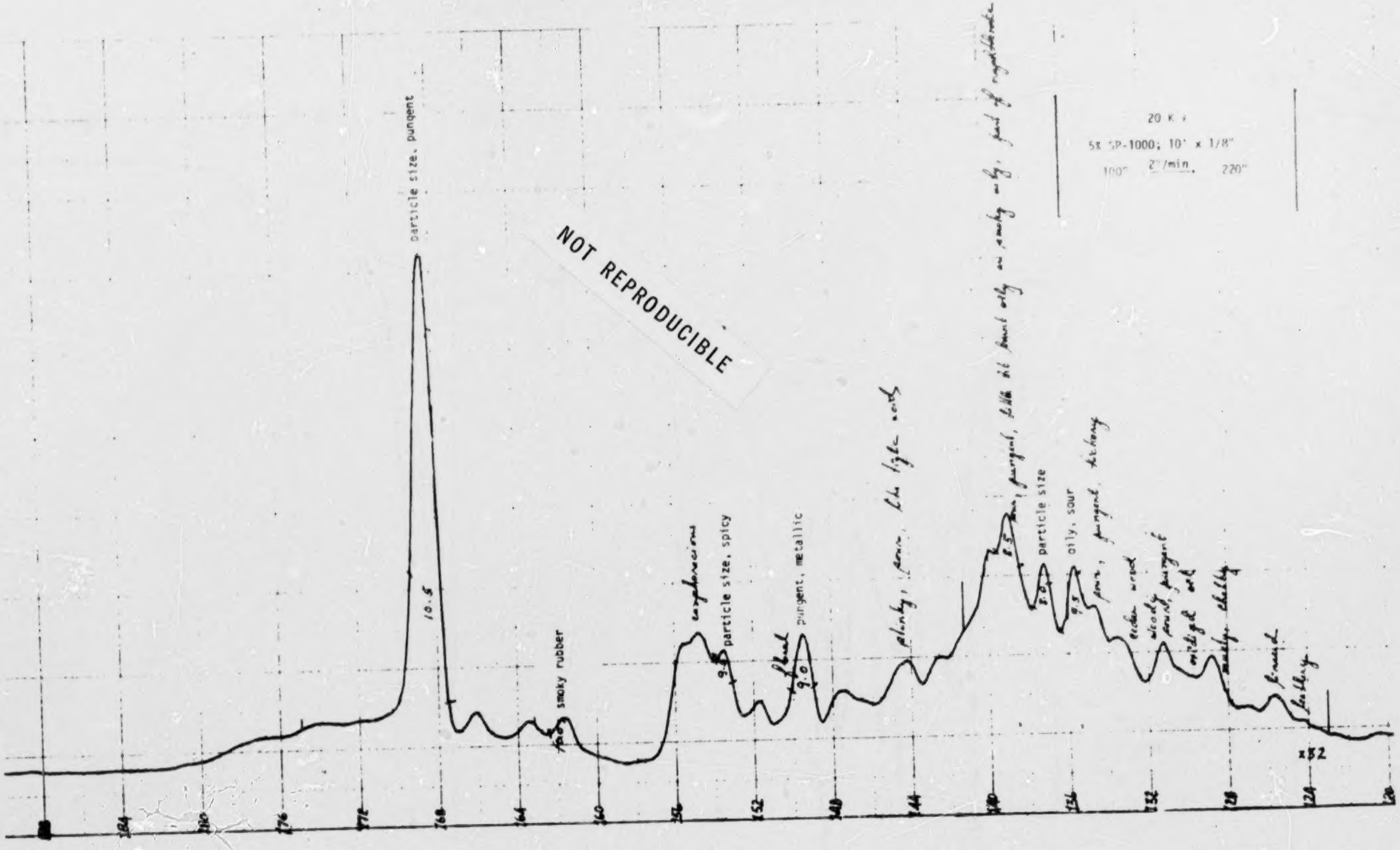

Figure D-7 CARBOWAX CHROMATOGRAM OF SILICONE PEAK 11 FROM SAMPLE 52C-34/5/6 AND 56C-39/40

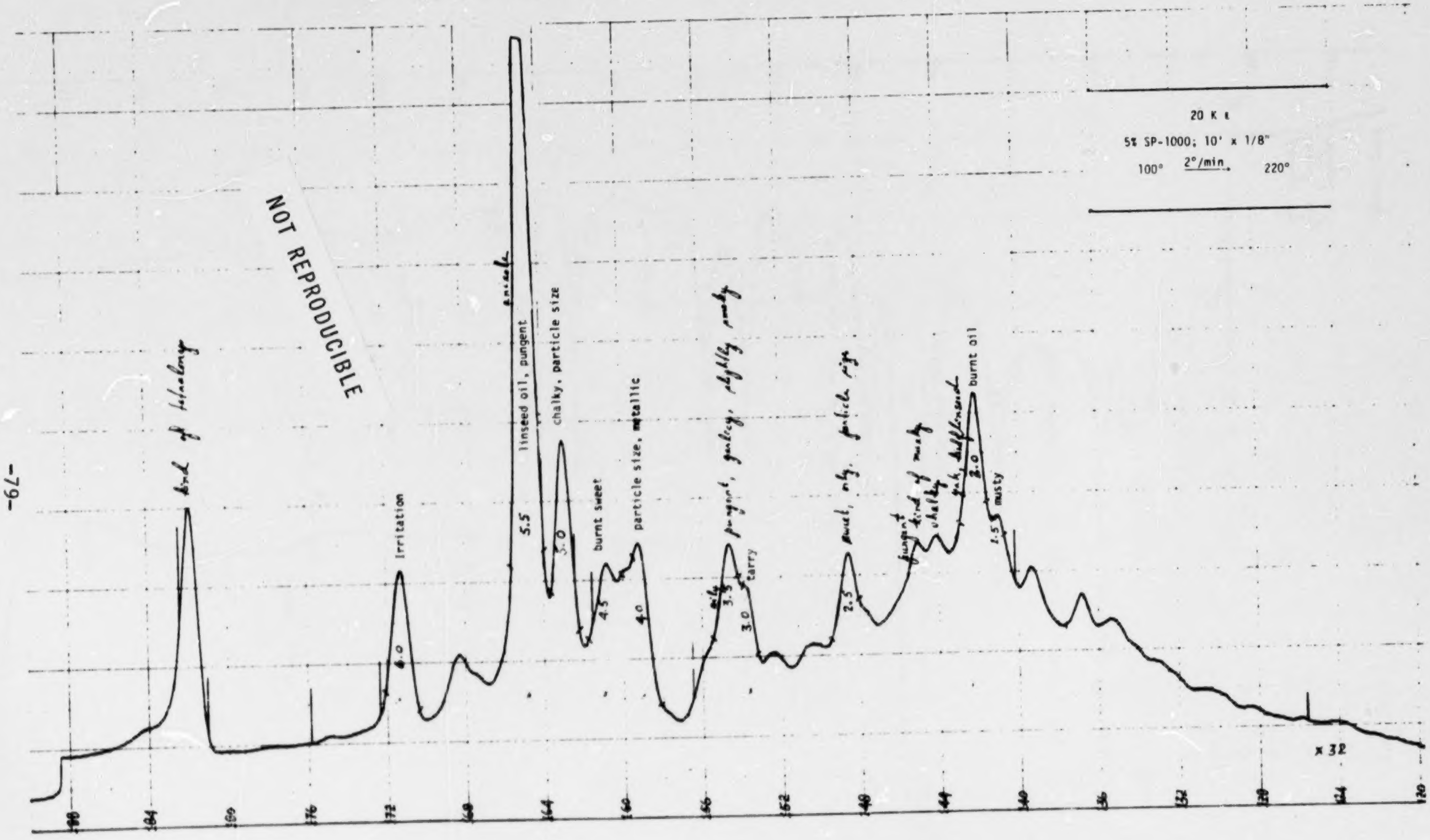

Figure D-8 CARBOWAX CHROMATOGRAM OF SILICONE PEAK 12 FROM SAMPLE 52C-34/5/6 and 56C-39/40

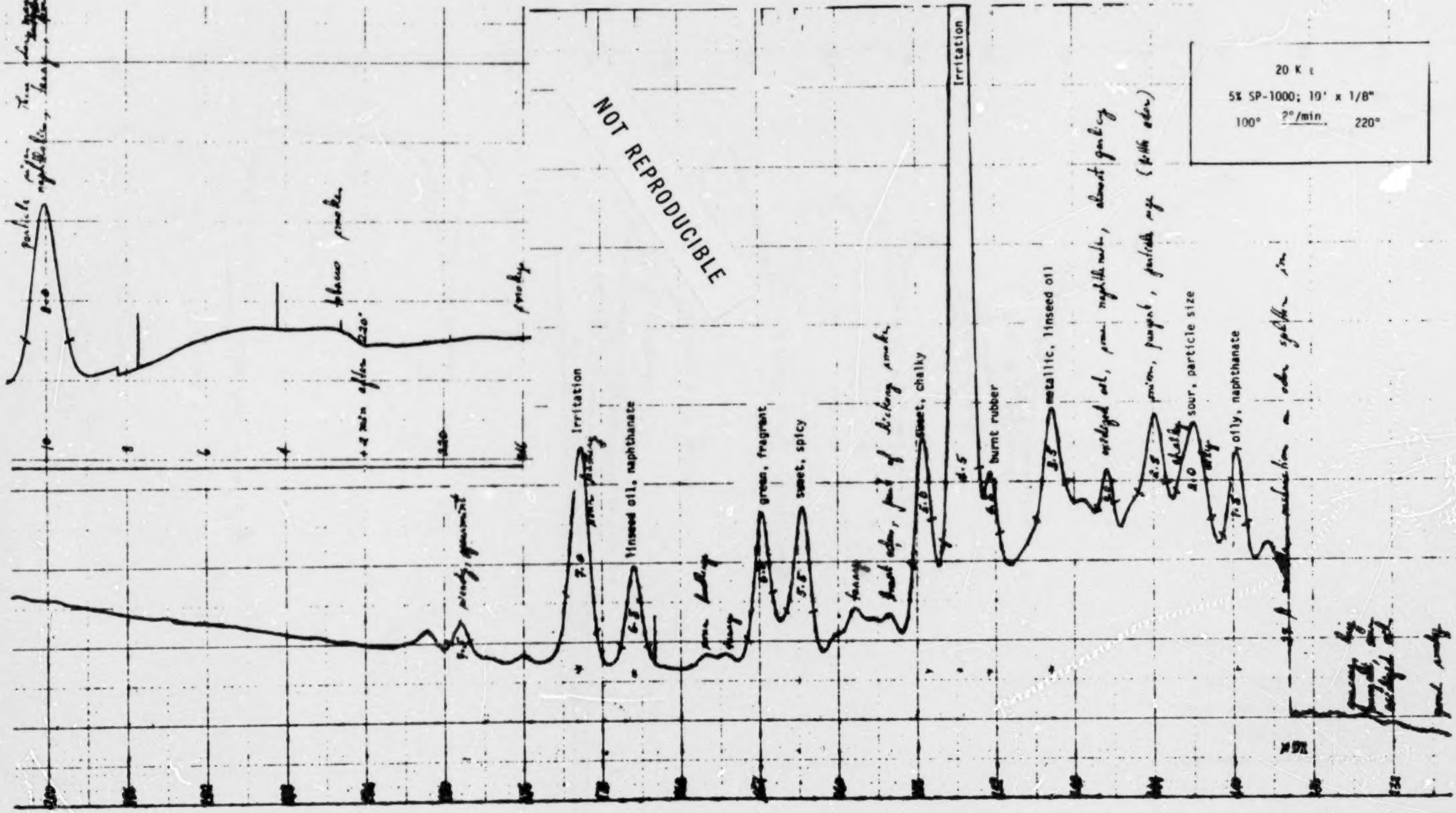

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Figure D-9 – CARBOWAX CHROMATOGRAM OF SILICONE PEAK 13 FROM SAMPLE 52C-34/5/6 AND 56C-38/40

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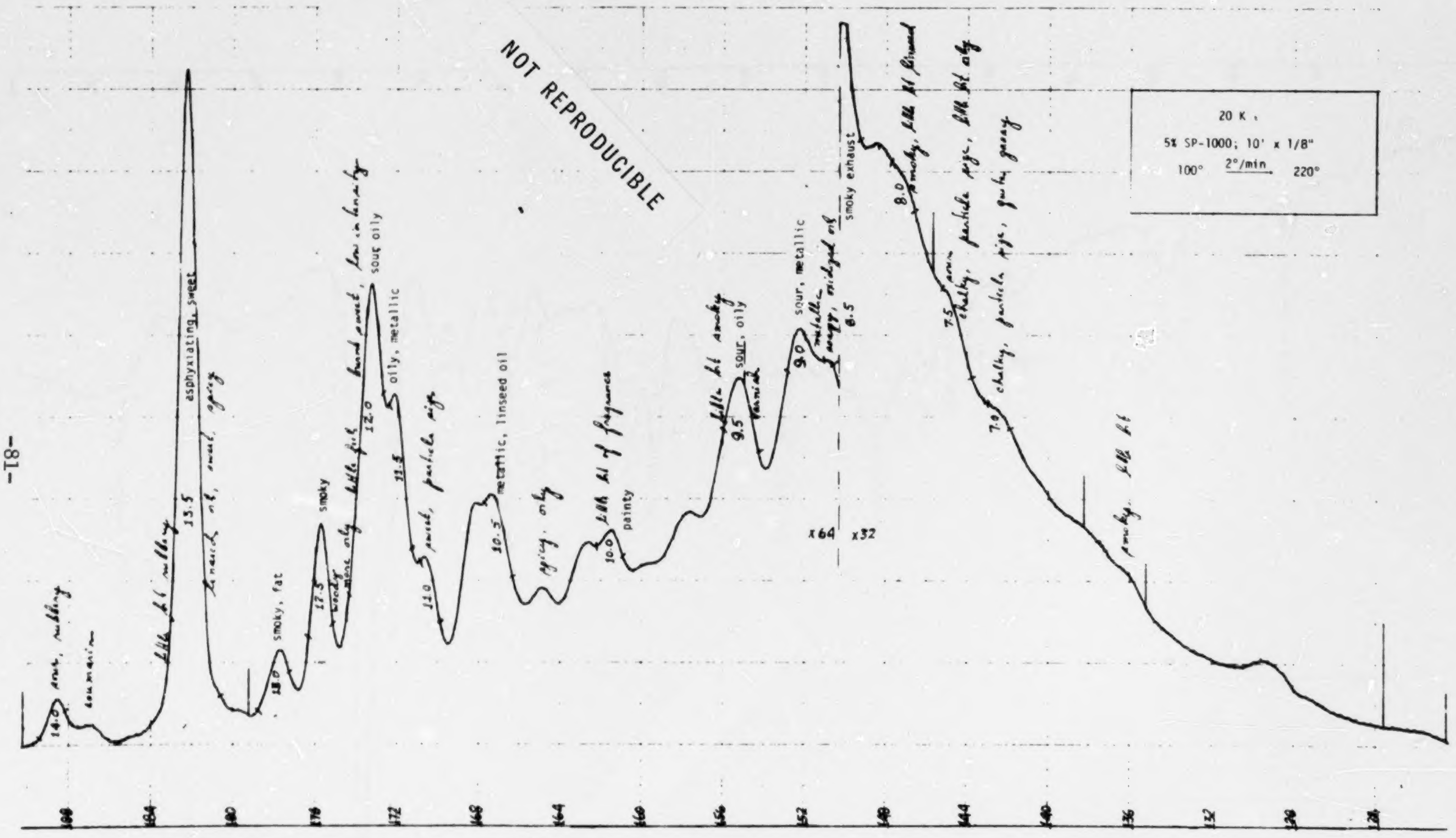

Figure D-10 - CARBOWAX CHROMATOGRAM OF SILICONE PEAK 14 FROM SAMPLE 52C-34/5/6 AND 56C-39/40

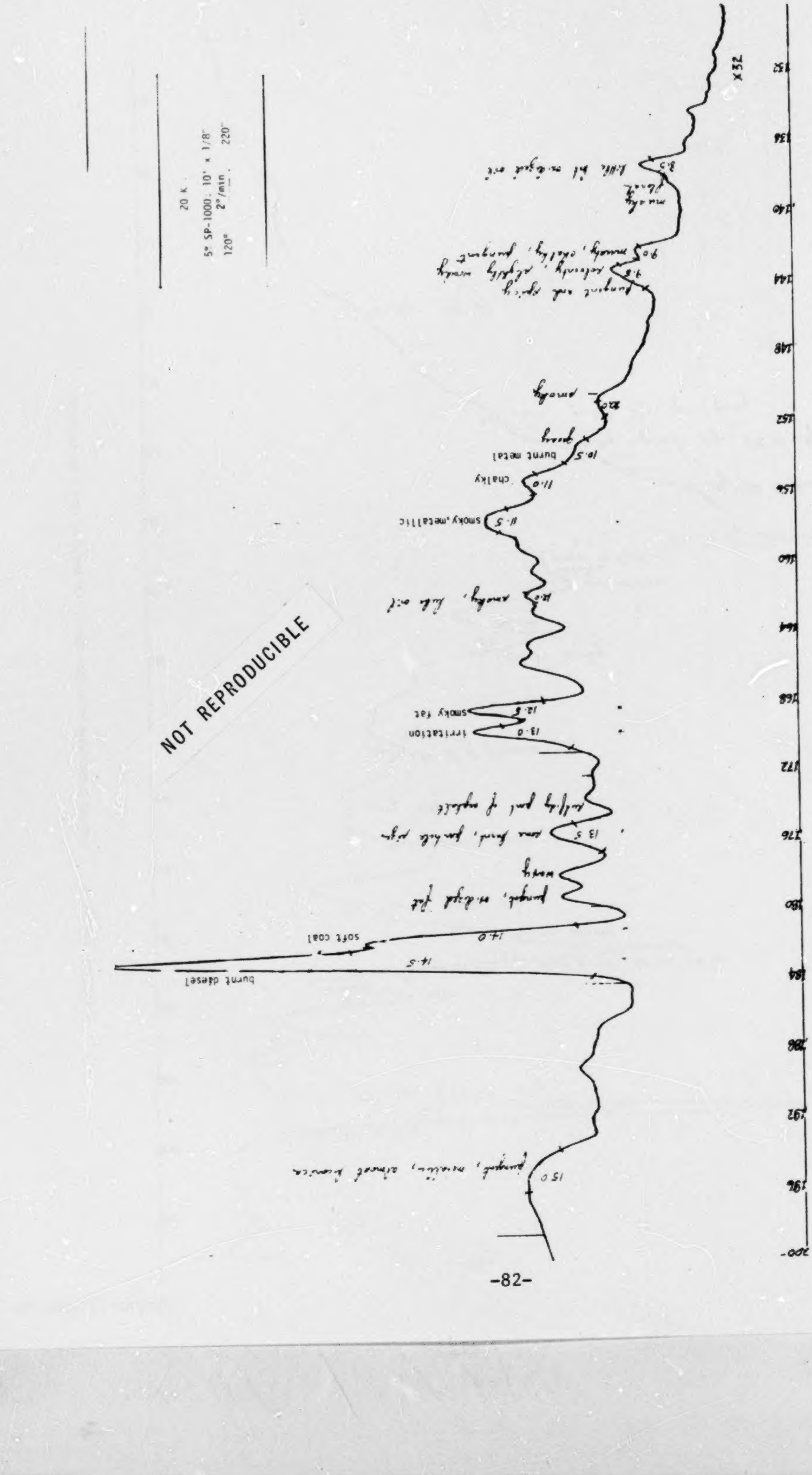

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Figure D-11 CARBOWAX CHROMATOGRAM OF SILICONE PEAK 15 FROM SAMPLE 52C-34/5/6 AND 56C-39/40

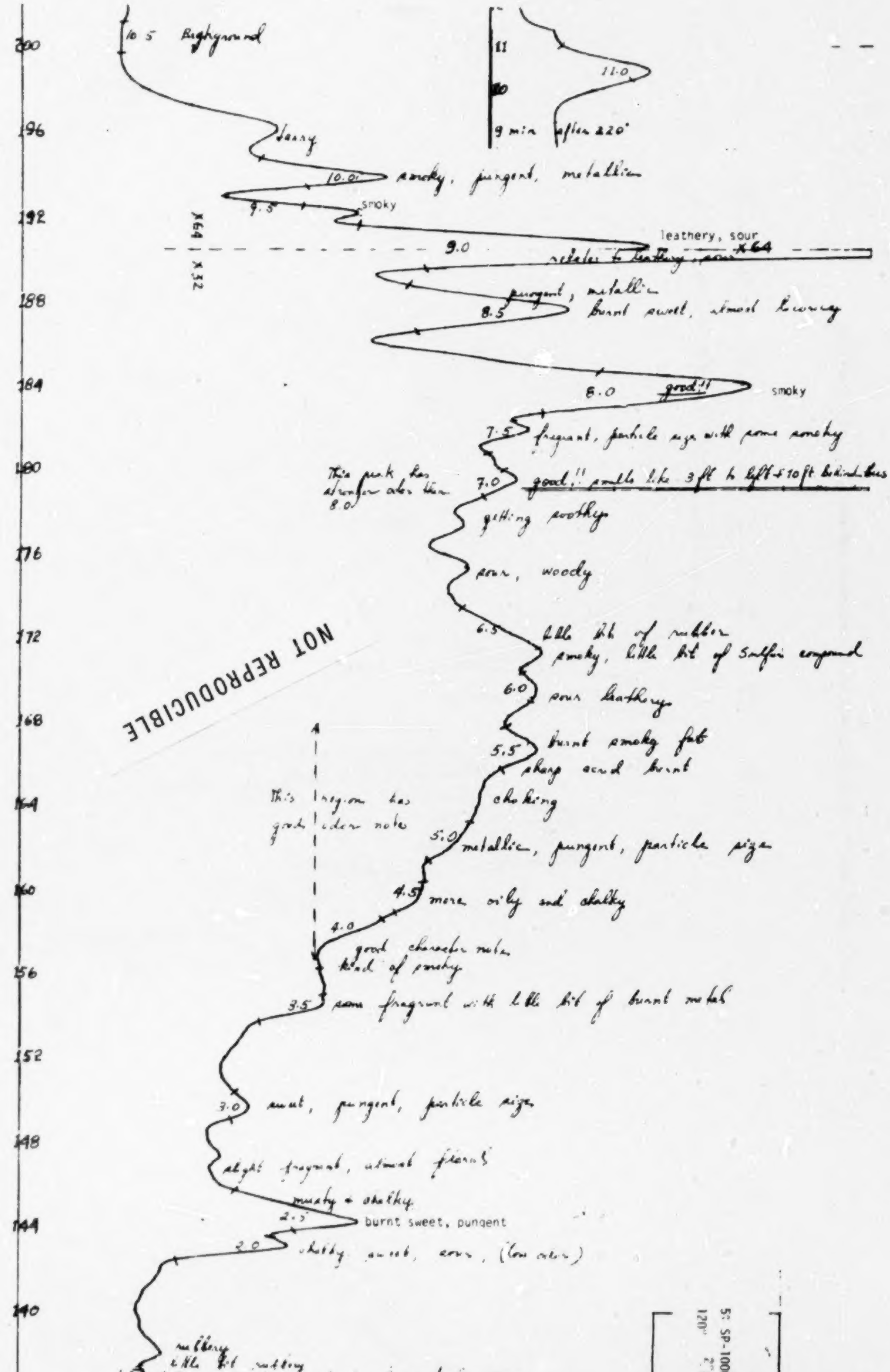

Figure D-12 CARBOWAX CHROMATOGRAM OF SILICONE PEAKS 16 & 17 FROM SAMPLE 52C-34/5/6 AND 56C-39/40

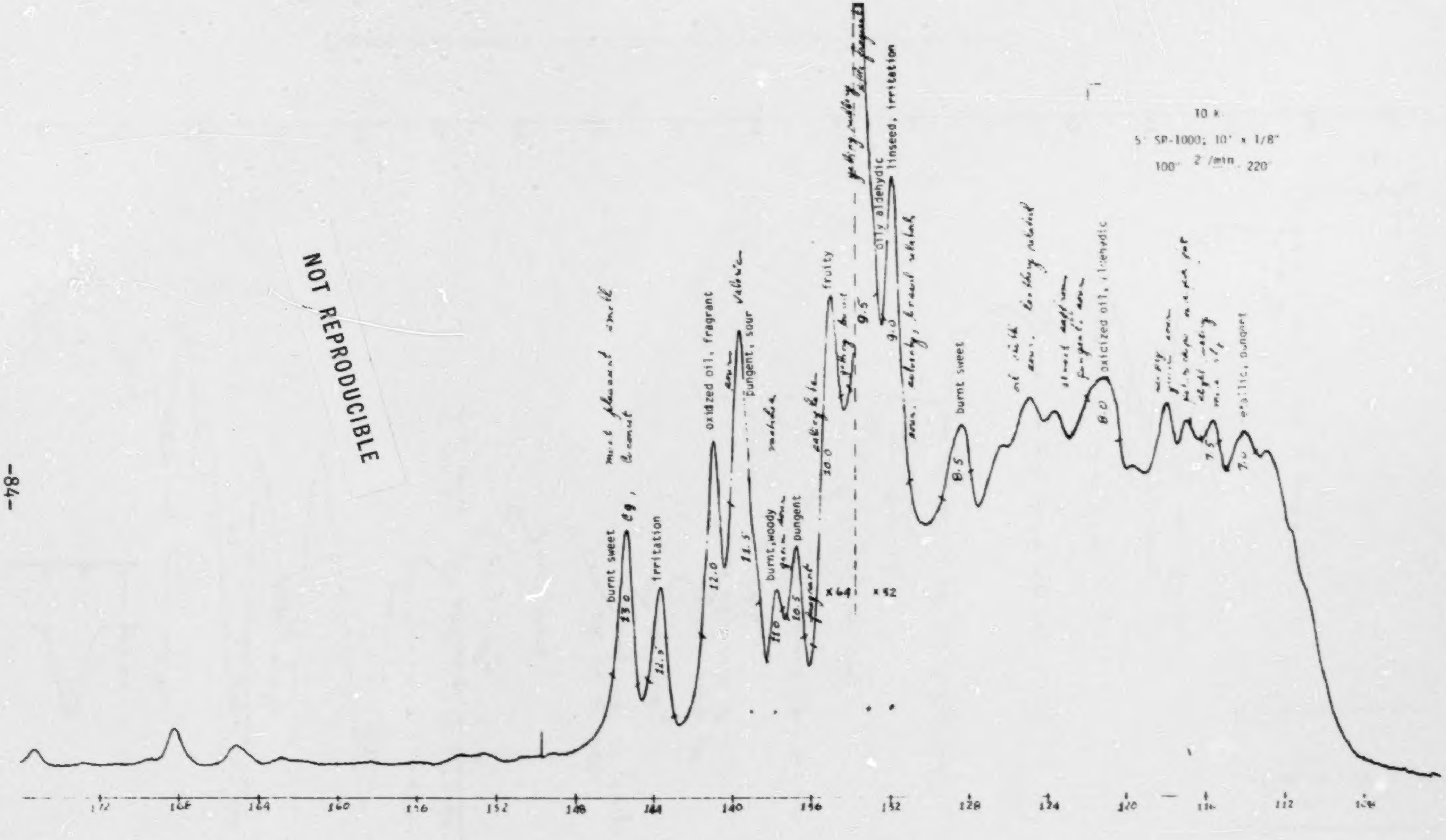

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Figure D-13 CARBOWAX CHROMATOGRAM OF SILICONE PEAKS 10 AND 11a FROM SAMPLE 56P-40

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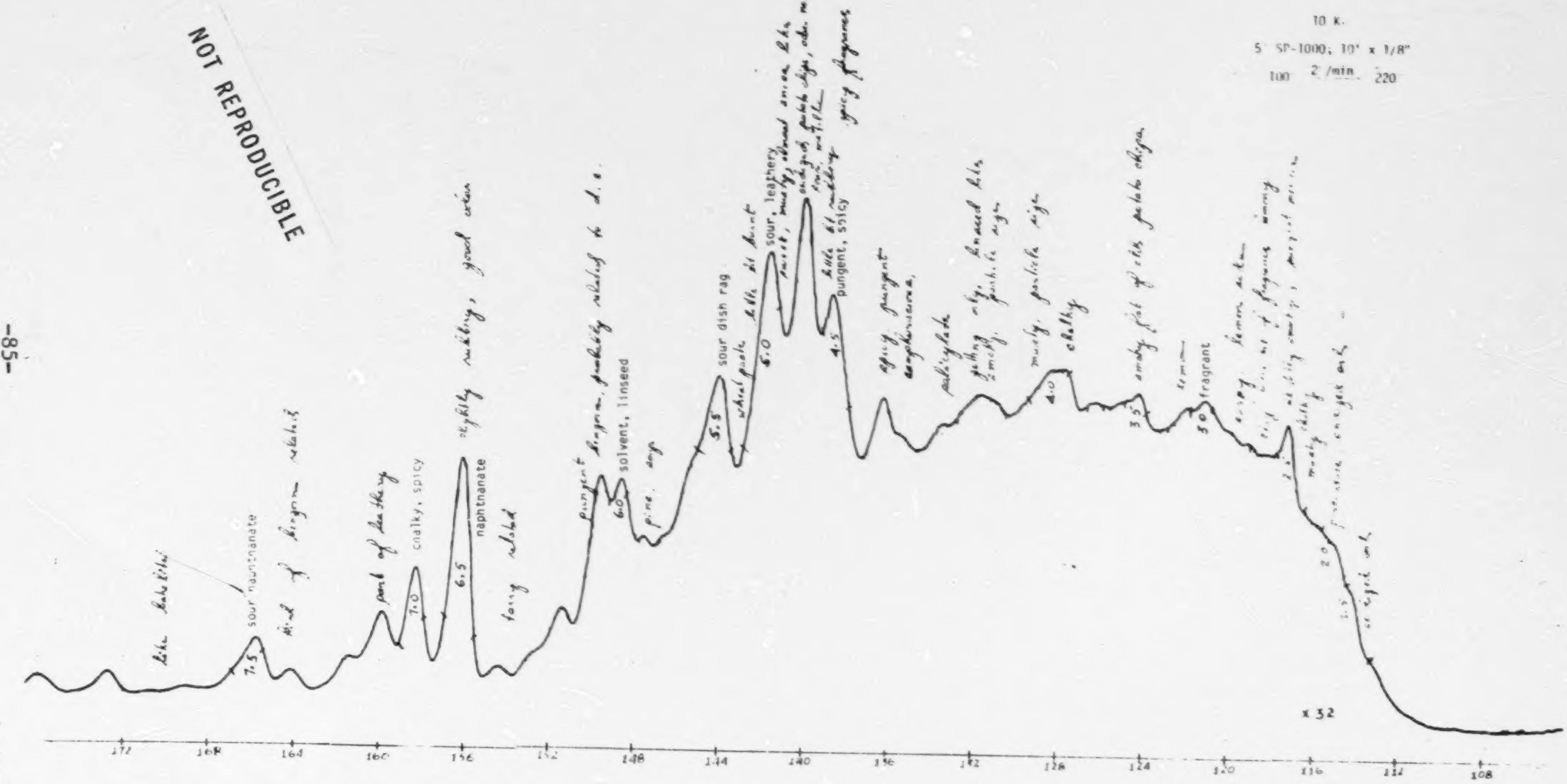

Figure D-14 - CARBOWAX CHROMATOGRAM OF SILICONE PEAKS 11b, 11c, and 12 FROM SAMPLE 56P-40

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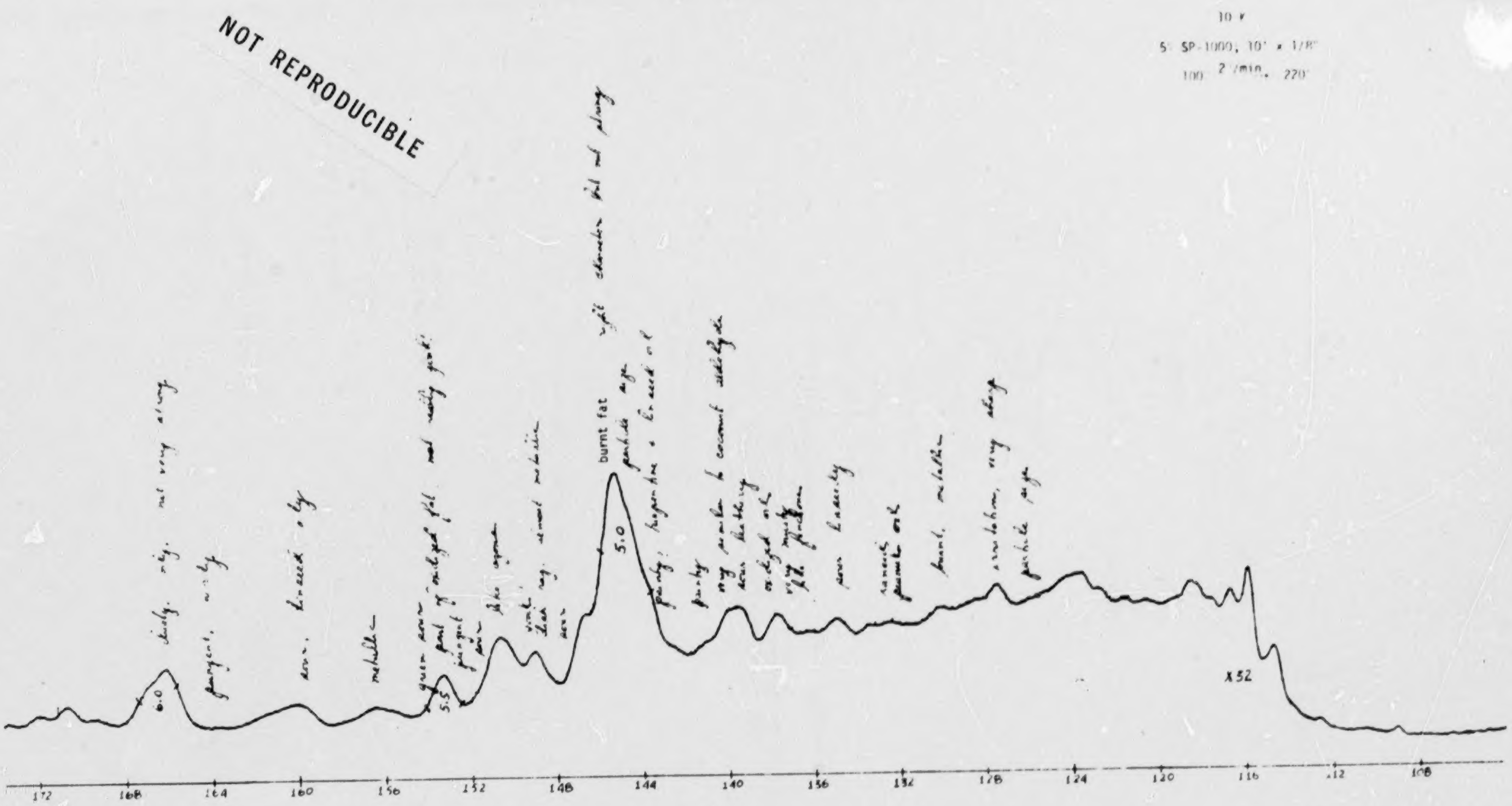

Figure D-15 CARBOWAX CHROMATOGRAM OF SILICONE PEAK 13 FROM SAMPLE 56P-40

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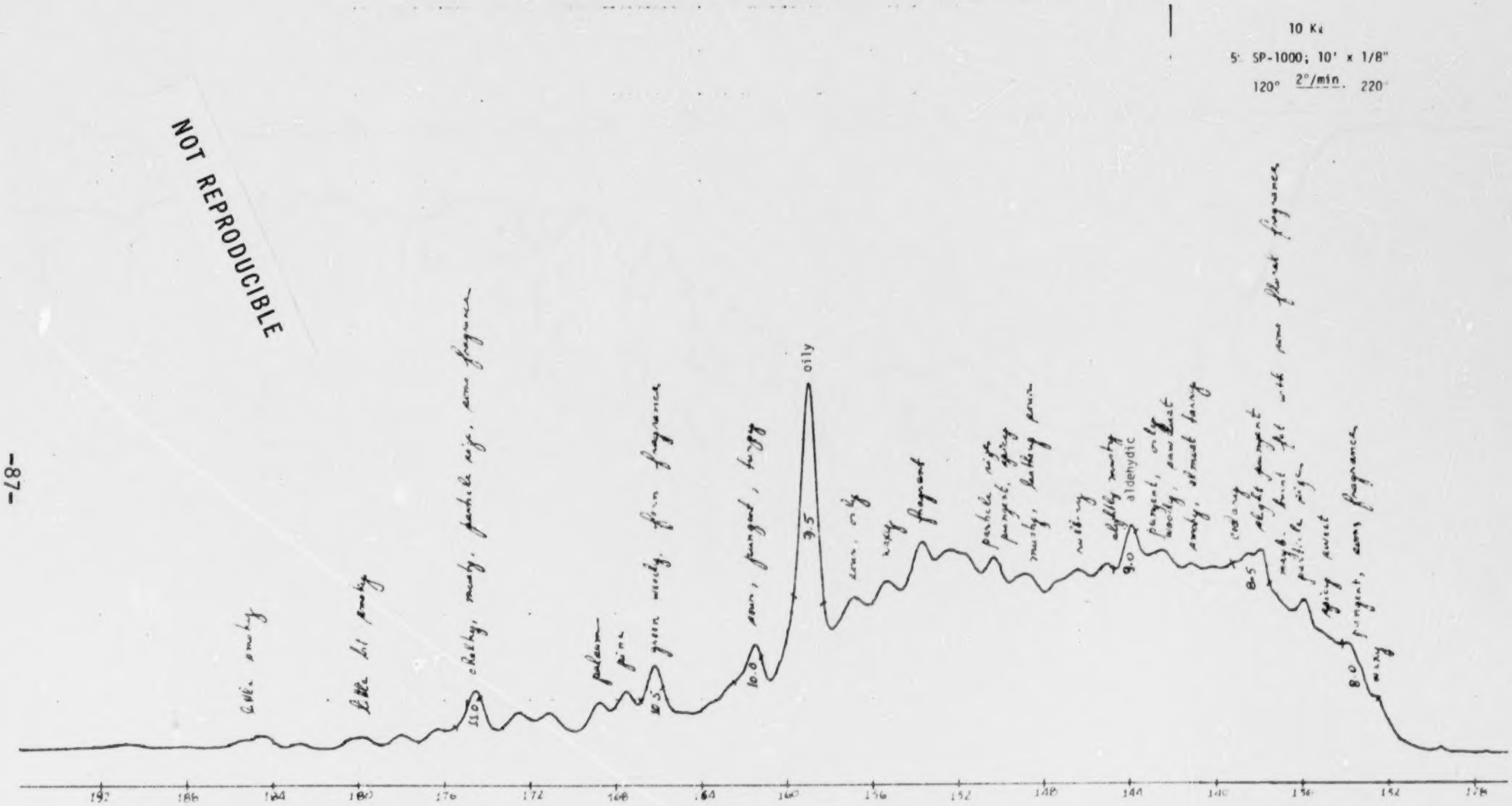

Figure D-16 ~~C~~ CARBOWAX CHROMATOGRAM OF SILICONE PEAK 14 FROM SAMPLE 56P-40

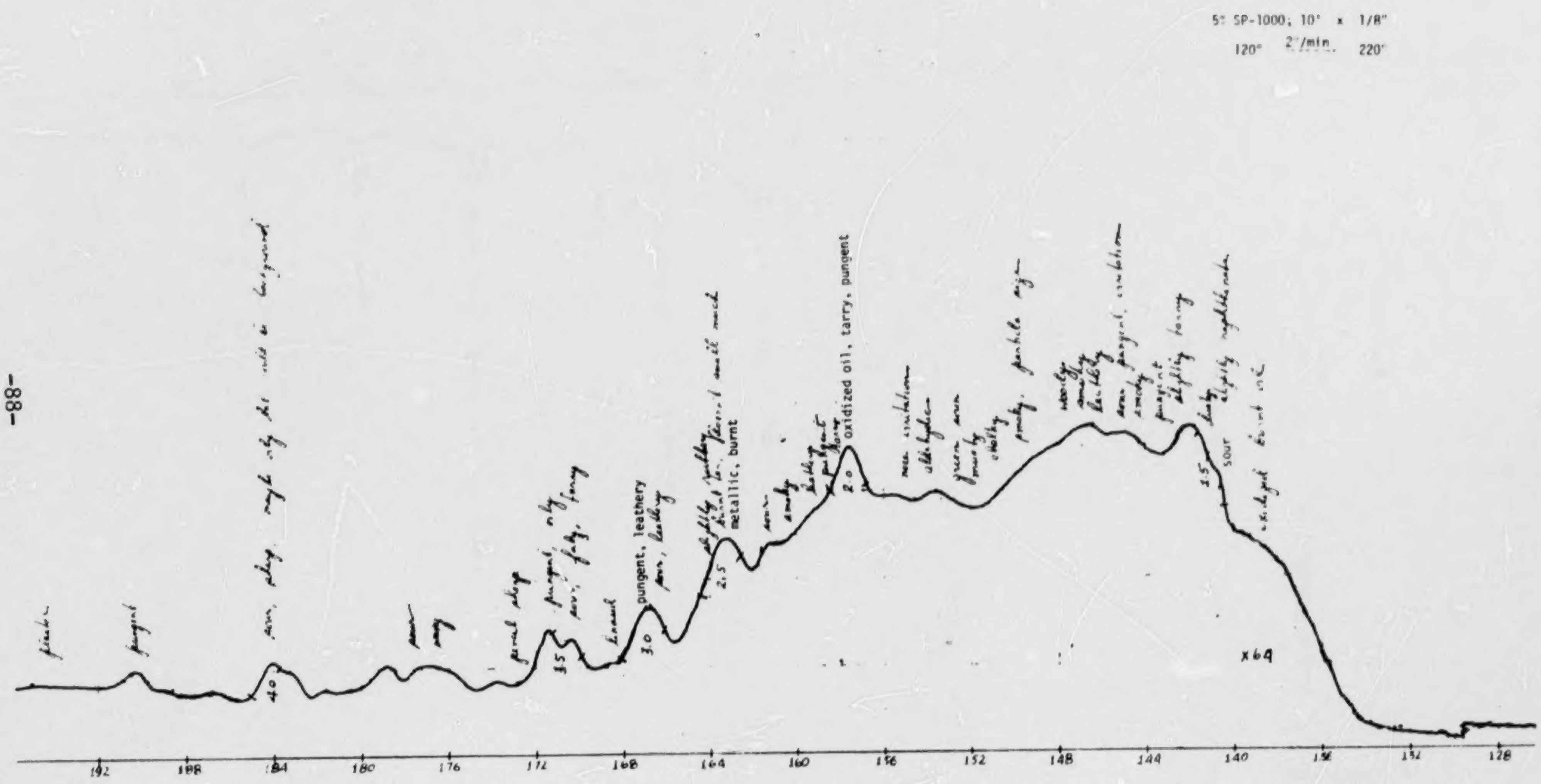

Figure D-17 CARBOWAX CHROMATOGRAM OF SILICONE PEAKS 15, 16, & 17 FROM SAMPLE 56P-40

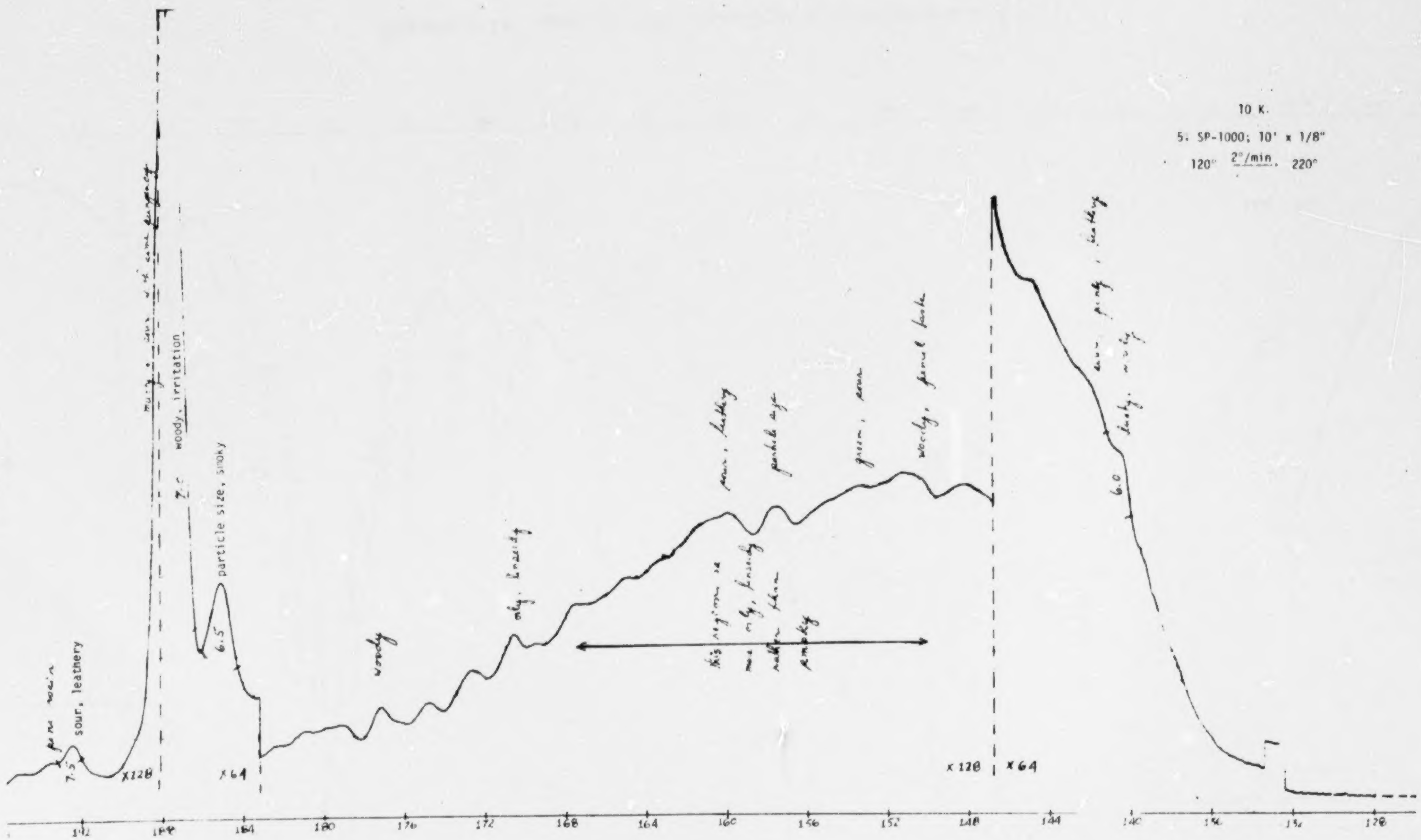

Figure D-18 CARBOWAX CHROMATOGRAM OF SILICONE PEAKS 18 & 19 FROM SAMPLE 56P-40

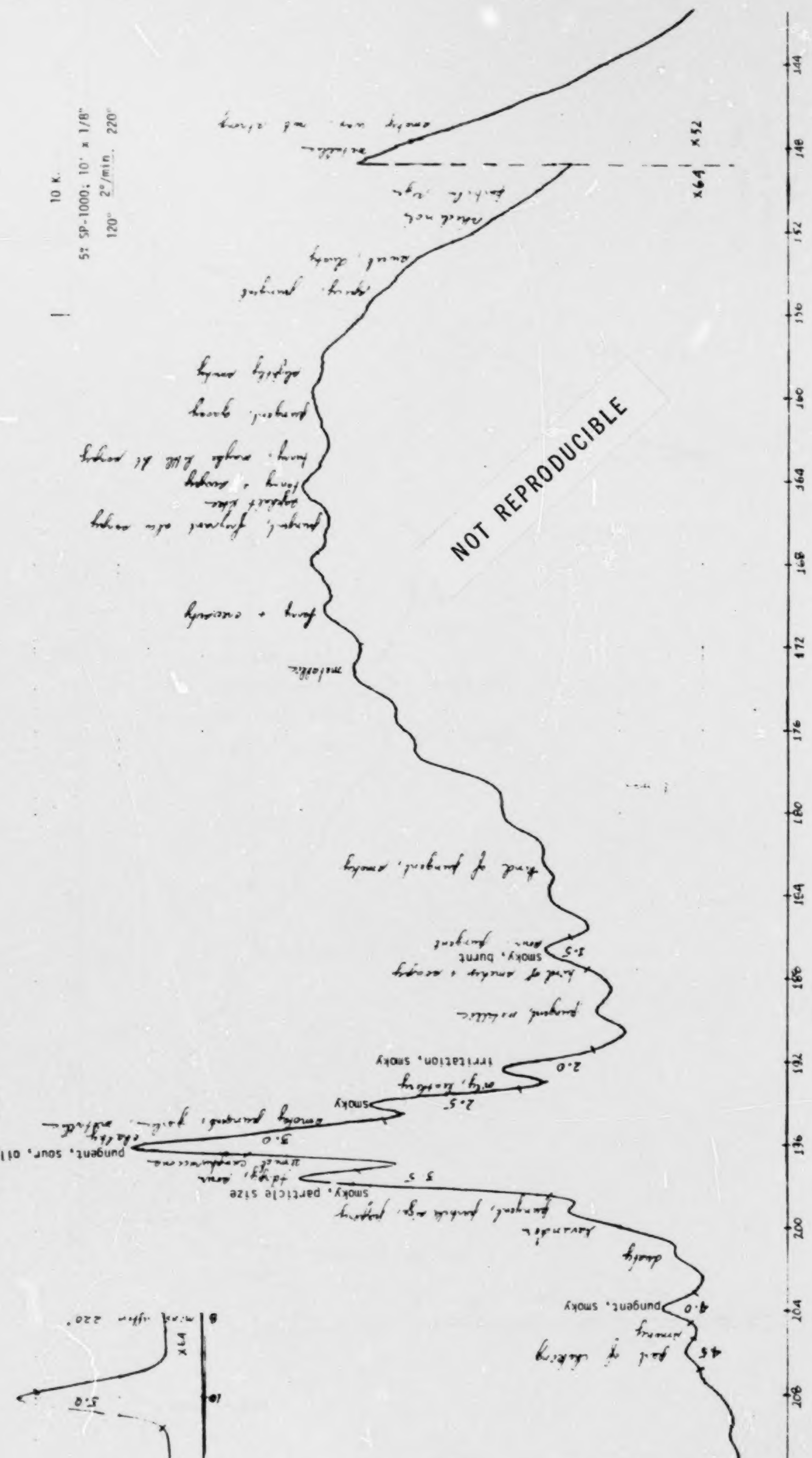

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Figure D-19 CARBOWAX CHROMATOGRAM OF SILICONE PEAKS 20, 21 & 22 FROM SAMPLE 56P-40

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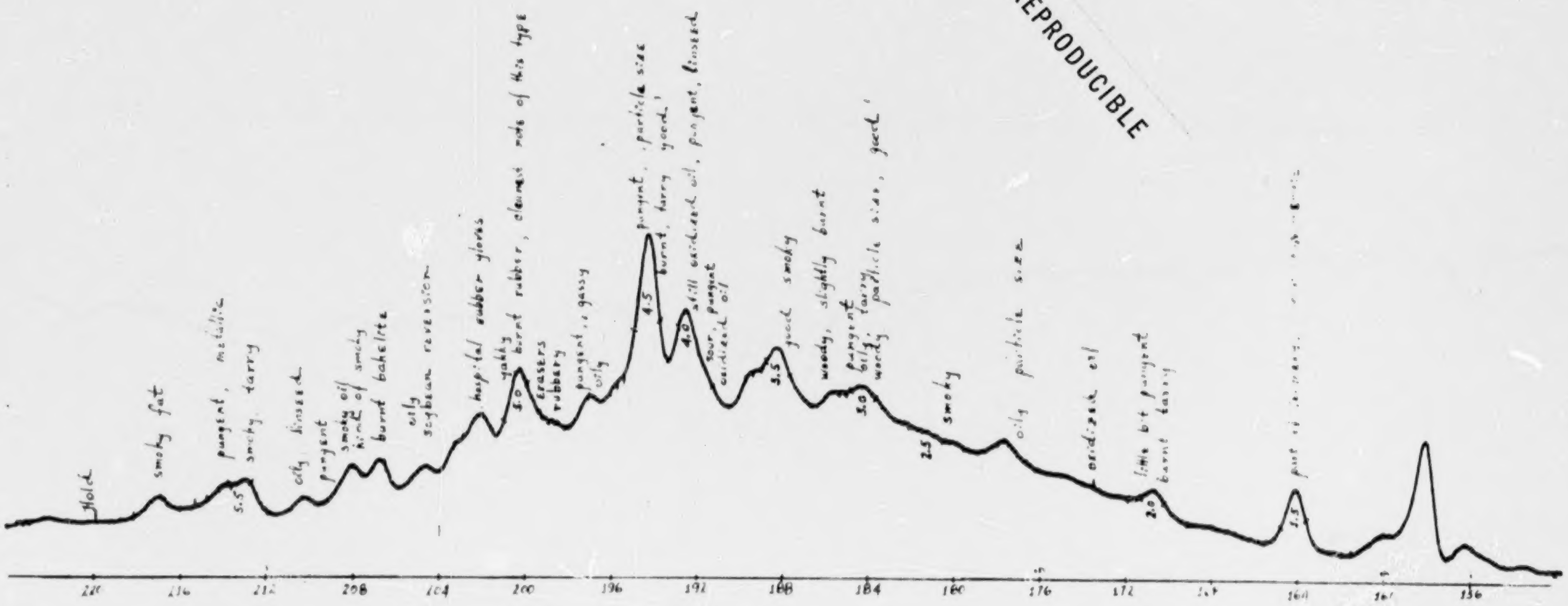

FIGURE D-20: CARBOWAX CHROMATOGRAM OF SILICONE PEAKS 18, 19 & 20 FROM SAMPLE 60 C-39/40/41

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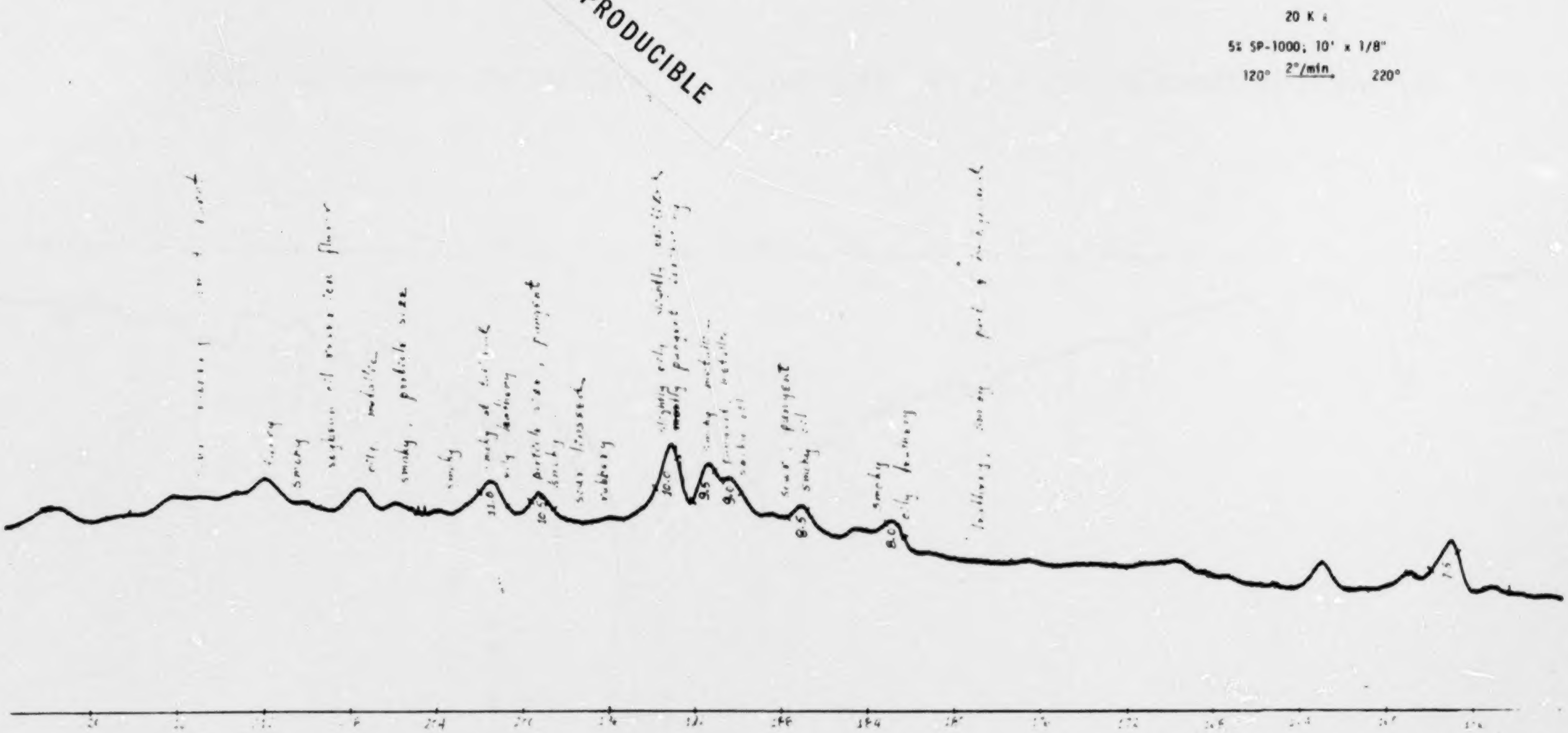

FIGURE D-21: Carbowax Chromatogram of Silicone Peaks 21 & 22 from Sample 60 C-39/40/41

APPENDIX E

STRUCTURE ASSIGNMENT METHODS

1. INTRODUCTION

The assignment of chemical structure type for the large variety of odorous materials observed in the oily-kerosene and smoky-burnt odor complex is a difficult task in view of the many choices possible. The purpose of this discussion is to present clearly in one place the various iterative processes used for assigning the selected structures for the various odor compounds.

2. DISCUSSION

Our chemical structure assignments have been made using as many of the following data sources as possible:

- Odor
- Gas Chromatography (GC)
  - Retention times on
    - Silicone OV-1
    - Carbowax SP-1000
- High Resolution Mass Spectrometry (HRMS)
  - Molecular weight (MW)
  - Elemental composition (ELCOMP)
    - (rings plus double bonds, R + DB)
  - Fragmentation pattern

It is important to remember that we were restricted to these sources of data due to the small amounts of sample available. Unfortunately, we have not always had all three sources of information available to use and more frequently have had to rely on HRMS and GC, HRMS and odor, or HRMS data alone. However, in each case, the objective has been to utilize all of the data available via an iterative process of interpretation-confirmation and structure choice refinement.

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Structure assignment for the oily-kerosene odor species was a considerably simpler task for the oxygenates in the smoky-burnt fraction for several reasons. First, there were only three or four principal structure types to identify, and they were tentatively rather easily selected on the basis of HRMS. Verification of these assignments was simplified in terms of the number of known reference chemicals which had to be studied. Another factor which was very important was the similarity of the identified species to the original fuel components - - therefore, allowing confirmation based on previously well known and documented reference information.

The task for the smoky-burnt oxygenates is a much more complicated one due to the greater number of structure classes possible. These data reported in Appendix F were interpreted using the data input described above to arrive at structure assignments. In several instances, it was possible to make specific structure assignments based on comparison with reference standards. In many instances, however, the structure class assignments are still tentative and continually in the process of being reevaluated as new data become available.

Generally, the first step was to restrict the possibilities as much as possible from the HRMS data (MW and ELCOMP). This process is discussed in detail in part 3 of this appendix. The rings plus double bonds (R+DB) approach has been a considerable aid in organizing this task. Detailed assignment of the geometric structure and functional groups then required extensive use of all possible available reference data.

The next step was to find or generate data on the physical properties or reference standards selected on the basis of the initial HRMS interpretation. Gas chromatographic reference data were obtained on the OV-1 silicone and SP-1000 Carbowax columns, and these data served as reference points for the identified exhaust species. The reference GC data were used first for establishing the presence of the specific reference standard compound in the exhaust sample when a match was achieved between the two sets of GC data and the HRMS data from the exhaust sample and reference study.

However, but of equal importance, was the use of the GC data to establish characteristic elution patterns for homologous series within a structure class and to characterize the differences, when they existed, between structure classes. This latter approach is probably most important because of the exceptionally large effort that would be required to confirm identifications based only on specific reference compound matches, due to the many homologues and isomers possible.

In addition to information found in general references on the combustion processes and products of paraffinic and aromatic hydrocarbons, structure assignments, based on the HRMS data for each species, have been aided by interpretation of the fragmentation patterns with particular reference to the work published by McLafferty (3) and

Budzikiewicz, Djerassi, and Williams (4). When available, the spectra were compared with the reference spectra published in the compilation by Cornu and Massot (5) and the AWRE set of spectra (6). In addition, valuable assistance was found in comparing the analysis of wood smoke by Lustre and Issenberg (7) and liquid smoke solution by Fiddler, Doerr, and Wasserman (8).

Finally, confirmation of structure class assignments were obtained by odor studies of the reference standards. These studies have confirmed the odor significance of several structural types. The studies are significant both in terms of odor differences between compound classes and also in detailing the effects of geometric isomerism on odor characteristics.

Most of the arguments presented above work also, of course, for the exclusion of certain structure types either on the basis of their GC or HRMS data and in that manner also help reduce the number of possibilities one needs to consider.

Several examples are shown in Table 1 to demonstrate the nature of the data available and the manner in which it was used to arrive at chemical structure assignments.

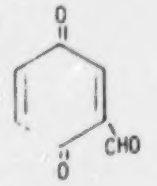
Table E-1

STRUCTURE ASSIGNMENT EXAMPLES

Observed/Assignment	OVT	SPT	MW	ELCOMP	R+DB	FRAGMENTS	Comment
Specific Reference Standard Match							
1. 52C/56C Peak 9	116	160	108	C_7H_8O	4	107(-H)	
m-Cresol	114	164	108	C_7H_8O	4	matches	
2. 52C/56C	140	160	132	C_9H_8O	6	131(-H), 103(-CHO)	
cinnamaldehyde	148	160	132	C_9H_8O	6	matches	correction of original assignment as indenol
3. 52C/56C Peak 13	140	158	132	C_9H_8O	6	104(-CO)	
indanone	150	160	132	C_9H_8O	6	matches	confirmation, structure first assigned on basis of HRMS
Assignment based on HRMS and extrapolated GC							
60C Peak 18-20	166	194	134	$C_9H_{10}O$	5	133(-H), 119($-CH_3$)	
allyl phenol	-	-	134	$C_9H_{10}O$	5	matches	consistent with lower derivative of dimethyallylphenol which elutes in region of peak 23, SPT 191°
Assignment based on HRMS data							
1. 52C/56C Peak 9 alkyl(butyl)furan	116	124	124	$C_8H_{12}O$	3	109,96,95 82(C_5H_6O)	spectrum consistent with butyl chain fragmentation both to eliminate C_2H_4 to give 96 and straight cleavage terminating in stable furan ring (82).
2. 52C/56C Peak 11 "benzaldehyde" actually, methyltolylketone	126	137	134	$C_9H_{10}O$	5	119($-CH_3$) matches reference	elutes too soon from Carbowax to be an indanol

Rejected possibilities

1. Tentative assignment of hydroxybenzoic acid to MW 138(5) $C_7H_6O_3$ species observed in 52C/56C Peak 10 rejected because reference standard acid exceded observed Carbowax elution temperature (standard SPT > 220°, exhaust species SPT 152°). Structure still unassigned.
2. The following quinone structure was considered for MW = 136 (6) $C_7H_4O_3$ species observed in 52C/56C peak 13 but rejected because HRMS pattern did not possess required ions for loss of C_2H_2 and C_3H_2O;



3. INTERPRETATION OF MASS SPECTRAL DATA

One of the most useful first interpretative aids in restricting the possible structural assignments are the R + DB values listed in the appendix tables. R + DB stands for "rings plus double bonds" and is an interpretive aid taken from McLafferty's treatment of mass spectral data (3). Values of R + DB are basically arrived at by a simple analysis of the degree of unsaturation in a molecule with a particular composition. For species containing only carbon, hydrogen, and oxygen the values are arrived at numerically from the formula

$$R + DB = \text{No. C atoms} - \tfrac{1}{2}(\text{No. H. atoms}) + 1$$

Several examples will serve to demonstrate the utility of the values:

for an n-paraffin C_6H_{14}

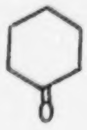
$R + DB = 6-7 + 1 = 0$; i.e., the n-paraffin has no rings nor double bonds

for a hexenone $C_6H_{10}O$

$R + DB = 6 - 5 + 1 = 2$; fitting a structure

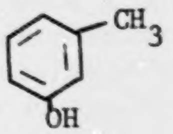
$CH_3\text{-}CH_2\text{-}CH_2\text{-}CH = CH\text{-}CHO$

Cyclohexanone also satisfies the R + DB criteria having one ring and one double bond.



a phenol C_7H_8O would have

R + DB = 7 - 4 + 1 = 4 consistent with the structure



These R + DB values serve to simplify the process of assigning structures while examining a multitude of data because they conveniently exclude certain possibilities in a manner easy to remember once one becomes accustomed to the procedure. Thus, in a trivial case, an R + DB = 7 species cannot be a paraffin, simple ketone, etc. The values do not imply certain explicit structures but only serve to restrict the possibilities. As the R + DB value increases, the structural possibilities expand considerably as one can find continuing new ways to combine aromatic rings, carbonyls, etc.

We have compiled in Table E-2 some possible hypothetical structure types which we feel are most likely, on the basis of our data so far, to be considered in the smoky-burnt diesel odor complex. The table is organized by R + DB for structures containing one, two, and three oxygen atoms. The data are self-explanatory for the most part, but several points to note are that alcohols are represented by -ols, ene refers to an unsaturation, carbonyls (or -ones) may be aldehydes and/or ketones, and hydroxy and methoxy derivatives are occasionally referred to as -oxy.

The table is meant to indicate primarily what new species may be considered as the R + DB value increases and does not exclude the combination of lower R + DB value functionalities. For the O_2 and O_3 cases, a dydroxy or methoxy derivative of an O_1 case is always also allowed. R + DB values are a routine output in the HRMS computer routines for each ion whose composition is listed.

TABLE E-2

POSSIBLE OXYGENATES - O_1-

R + DB	Possible Structure Type
0	alcohols (C_1) *, ethers (C_2)
1	ketones (C_3), aldehydes (C_1), cyclic-ols (C_5), epoxides (C_2)
2	alkenones (C_3), cyclic carbonyls (C_5)
3	dienones (C_5), cyclic-ene-carbonyls (C_5), furans (C_4)
4	phenols (C_6), benzyl alcohols (C_7)
5	phenyl carbonyls (C_7), indanols (C_9), allyl phenols (C_9), dihydrobenzofuran (C_8)
6	benzofurans (C_8), indanones (C_9), indenols (C_9), phenylene-carbonyls (C_8)
7	naphthols (C_{10}), indenones (C_9)
8	naphthaldehydes (C_{11})
9	dibenzofurans (C_{12})

---

* Carbon number in parenthesis represents smallest number of carbon atoms which first member in homolgous series may have.

Table E-2 cont........

POSSIBLE OXYGENATES - O_2

R + DB	Possible Structure Type
0	diols (C_2), peroxides (C_2), ethers (C_2)
1	acids (aliphatic) (C_2), esters (C_2), hydroxy carbonyls (C_4)
2	alkene acids (C_3), esters (C_3), cyclic acids (C_6), dicarbonyls ($_4$), oxy cyclo carbonyl (C_5)
3	MCP's (C_5), cyclodiones (C_5), oxy furans (C_4)
4	furfurals (C_5), hydroquinones (C_6), methoxy phenols (C_7)
5	aromatic acids (C_7), hydroxy aromatic carbonyls (C_7), oxy indanols (C_9), quinones (C_6), allyl phenols (C_9)
6	phenylpropene acids (C_9), dihydrocoumarins (C_9), aromatic dialdehydes (C_8), oxy benzofurans (C_8), oxy indanones (C_9)
7	coumarins (iso) (C_9), benzofurfurals (C_9), indandiones (C_9), oxy indenones (C_9)
8	naphthoquinones (C_{10}), hydroxy naphthaldehydes (C_{11})

Table E-2 cont..........

POSSIBLE OXYGENATES - 0_3

R + DB	Possible Structure Type
0	ethers (C_4)
4	dimethoxyphenols (C_8)
5	dioxyphenyl carbonyl (C_7), allyl phenols (C_9), oxy benzoic acids (C_7), oxy quinones (C_6)
6	oxy phenyl propene aldehydes (or oxy allyl phenyl aldehydes (C_{10})

(plus other hydroxy and methoxy derivatives from
0_1 and 0_2 categories)

4. GAS CHROMATOGRAPHIC DATA

Several adjustments are necessary in comparing the GC data for the exhaust and reference compounds to determine the degree of match of the physical properties. While the adjusted retention temperatures of the reference standards reported in Table 2 of this report are probably accurate to about 2°C, the exhaust sample data are not known with the same degree of accuracy. The peaks trapped from the silicone column were collected over a 3° - 12°C range, and the average temperature of the collection range was recorded. This spread, and the overlap between peaks, requires, therefore, that any reference standard eluting between ± 3 - 6° of the trapped OV-1 temperature be considered.

The reference standards adjusted elution temperature (SPT) were obtained on the SP-1000 Carbowax column using the 120°C initial 2°C/min 220°C hold program, while much of the exhaust identification work was done on other program rates. The relationship between the various Carbowax elution temperatures obtained by studying reference standards under each of the conditions is, however, a smooth one and by reference to Figure E-1, the exhaust data may be corredted to the same base as the reference standards. The correlation between peak number and elution temperature necessary for comparison of the exhaust and reference standard data is shown in Figure E-2.

We have attempted to organize our GC retention data so that one could differentiate between structure classes from these data in a simple manner. Unfortunately, establising characteristic GC elution patterns for the structure classes has not been as straightfoward as one would wish. The data plotted in Figure E-3 serve to illustrate this point. The figure represents the data available at this time on one of the structure groups we have studied most extensively, the phenols and methoxy benzenes. The elution temperature on the silicone column (OVT) are plotted against the Carbowax (SPT) temperature for the two related classes. While it is apparent that the free phenols as a group elute at a higher temperature on the Carbowax than the methoxy benzenes, there is a large spread in the data, and it is difficult to establish a simple correlation. These results are not unexpected since this type of correlation technique works best with increasing chain length homologous series, and the exhaust species vary principally by degree of substitution on an aromatic ring. The overlap of these data with other structure classes can be seen from a few other reference compounds also shown on the figure.

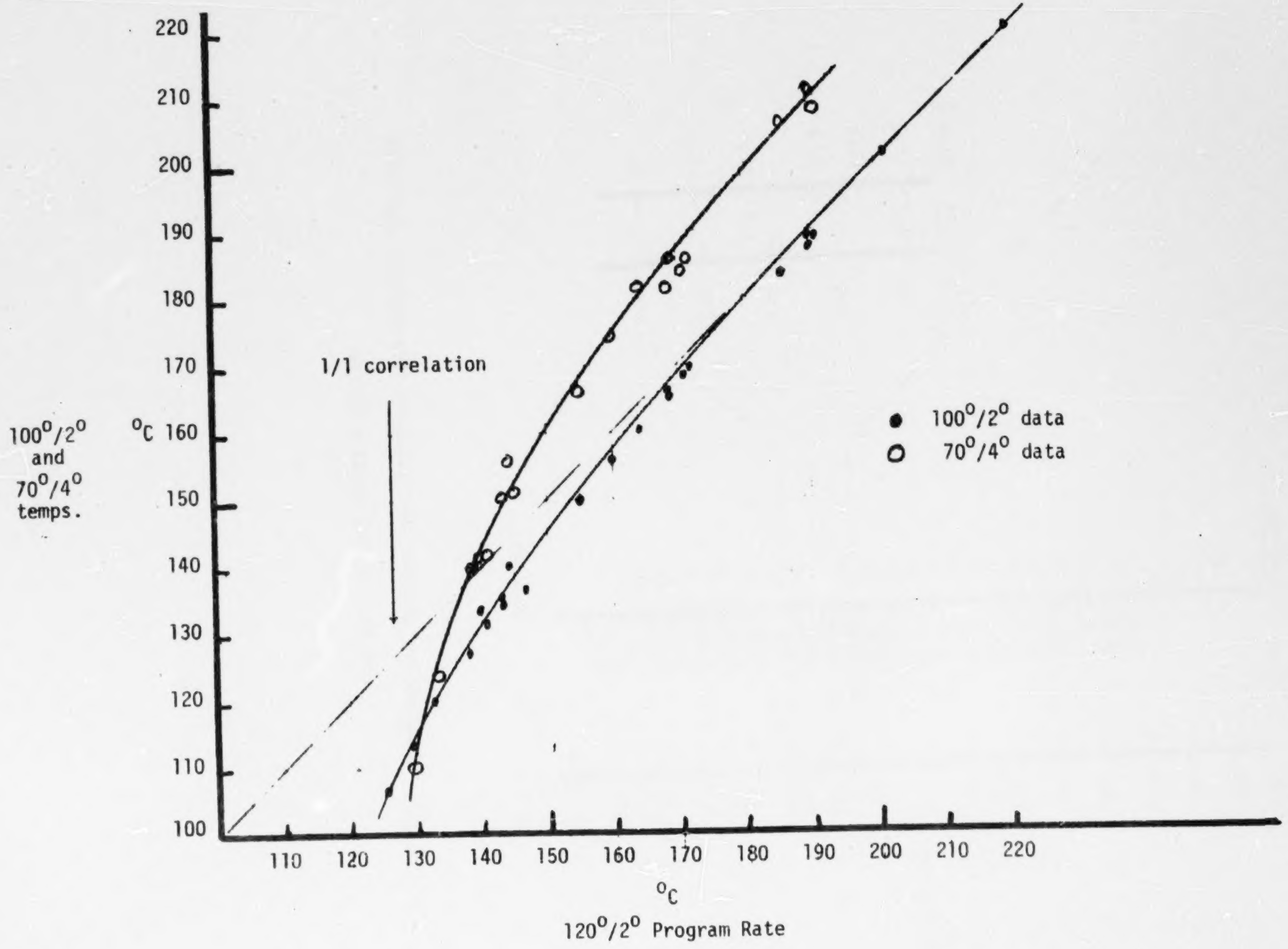


FIGURE E-1: TEMPERATURE RELATIONSHIP OF VARIOUS SP-1000 ELUTION PROGRAMS TO THAT FOR THE 120°/2° PROGRAM RATE

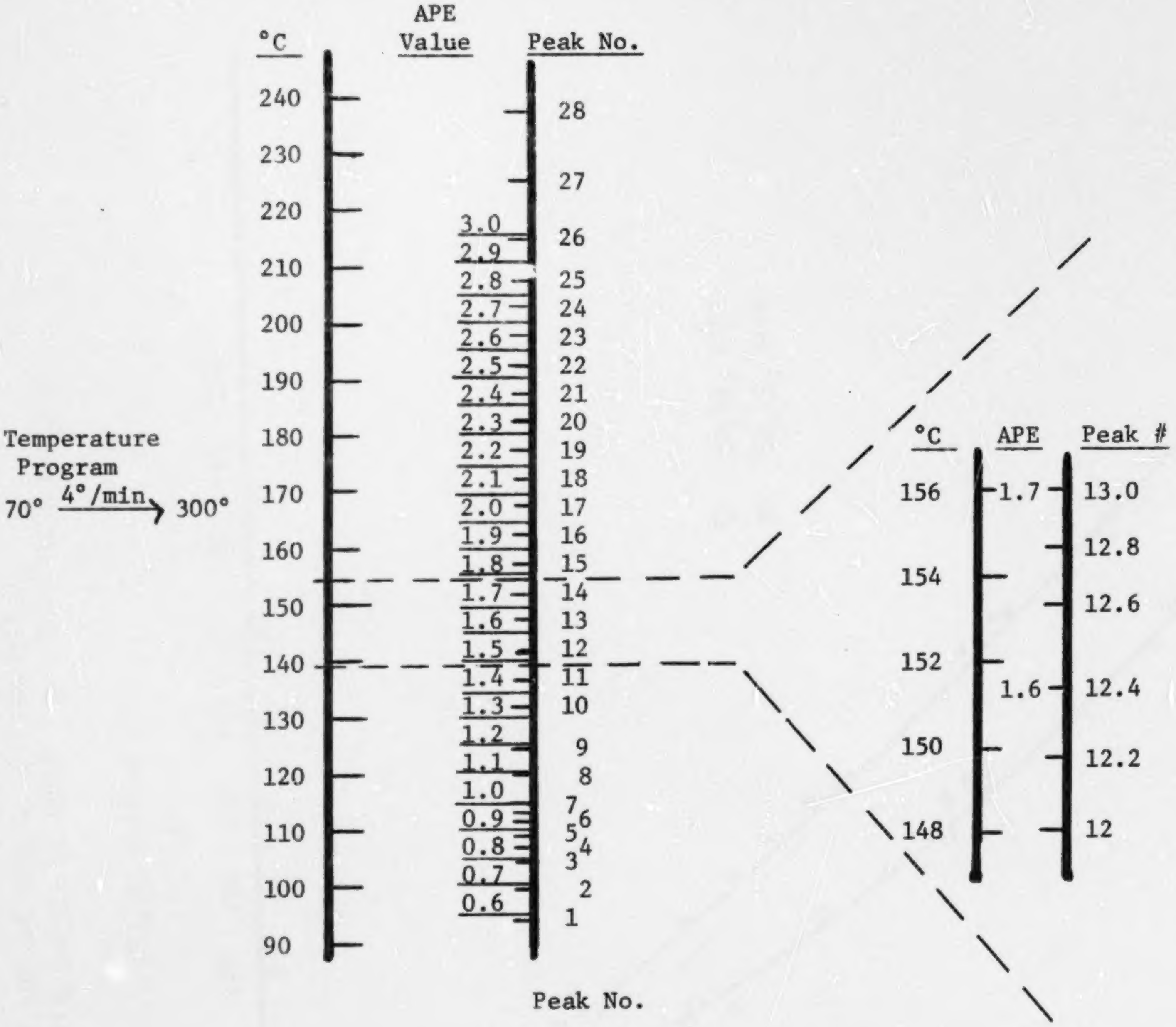


FIGURE E-2: RELATIONSHIP BETWEEN OV-1 SILICONE TEMPERATURE, APE VALUE AND PEAK NUMBER ELUTION SCALES

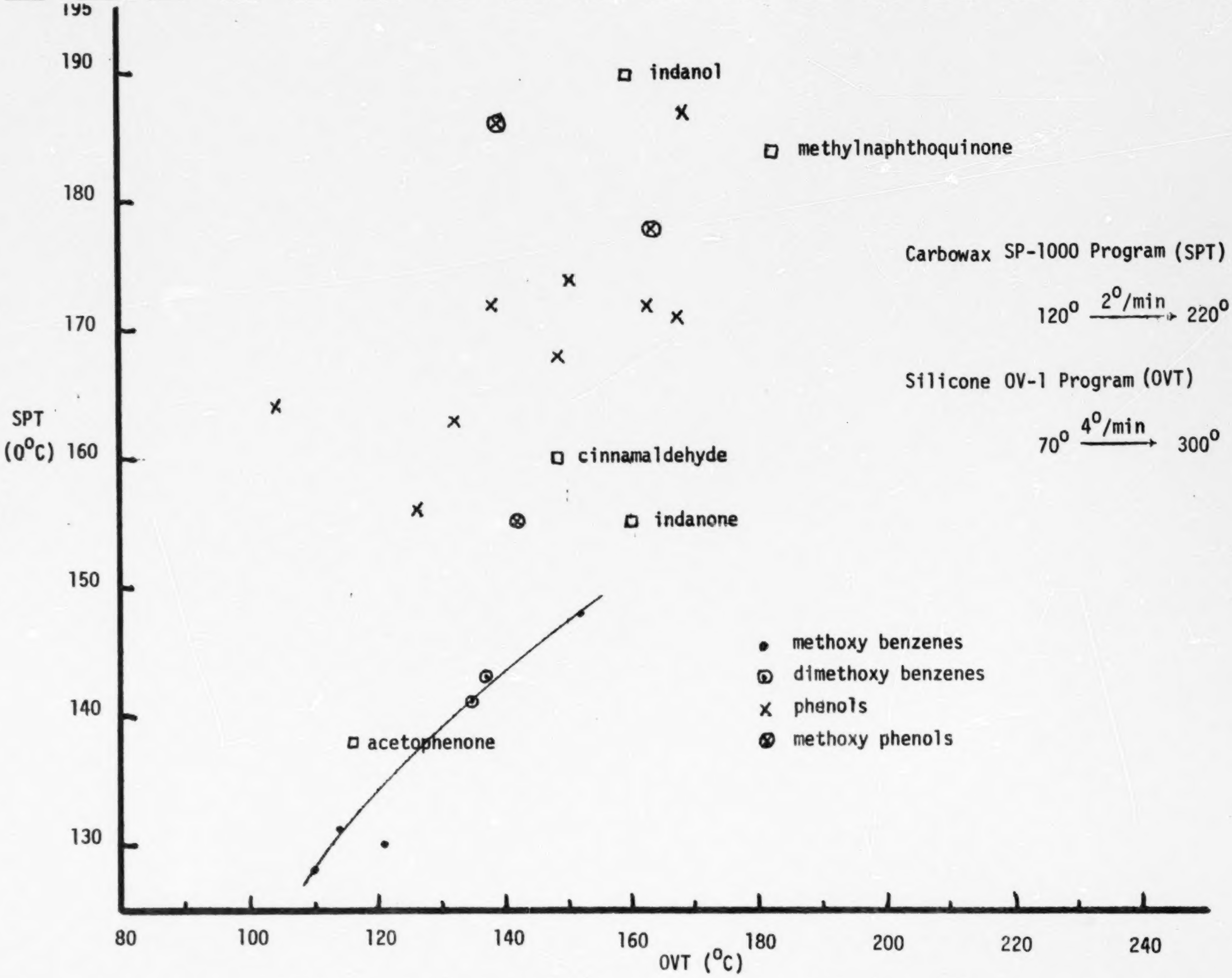


FIGURE E-3: ELUTION PATTERNS OF OXYGENATED REFERENCE STANDARDS ON SILICONE AND CARBOWAX GC COLUMNS

APPENDIX F

Basic High Resolution Mass Spectrometry-Odor Data on Odor Significant Smoky-Burnt Species

The data included in Tables F-1 to F-4 represent most of the basic information obtained in the structure-odor study of the three smoky-burnt samples 51C-34/5, 52C-34/5/6 plus 56C-39/40, 60C-39/40/41 and 56P-40.

The significance of each of the items in the tables is as follows:

The first line after the title states that

Peak 9 - The peak area trapped from the silicone (OV-1) column.

APE 0.8 to 0.9 - The silicone retention temperature relative to allyl phenyl ether.

OV 138° - 138 is the nominal eluting temperature (°C) on the OV-1 column of peak 9.

SP 70°/4° - The temperature programmed conditions used for the rechromatography of trapped peak 9 on the SP-1000 Carbowax column -- an initial temperature of 70°C followed by a 4°C/min program rate. For the sample run at the same program conditions used for the reference standards, i.e. from 120°C at 2°C per minute, a tolerance of ± 2°C has been allowed for the various peaks identified. For those traps which were run at the different program conditions, a larger tolerance value has been used; ± 6°C for 70 $\xrightarrow{4^{\circ}}$ 220°C and the 100 C $\xrightarrow{4^{\circ}}$ 220°C programs and ± 4°C for the 100 $\xrightarrow{2^{\circ}}$ 220°C program conditions.

The column headings have the following significance:

% - This number represents the relative amount of the particular species eluting on the Carbowax column as compared to the total original smoky-burnt sample.

Exp - The peak identification number of the species studied, the number corresponds to the photoplate exposure number.

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SPT - The elution temperature (°C) of the peak from the SP-1000 column adjusted to a standard program condition of an initial 120°C followed by a 2°C/min temperature program rate.

Odor - Observed odor characteristic of the eluting peak.

The molecular weight (MW) of the species measured by HRMS. R+DB is a structure interpretation air meaning "rings plus double bonds." The interpretive significance of the R+DB value is discussed in Appendix E.

ELCOMP - Elemental composition of the indicated molecular ion as obtained from the HRMS data.

Structure Type - Chemical structure of the measured species. In most instances, the indicated structure types represent our best present estimate of the most probable structure. In some cases sufficient supporting reference data are available to make definite assignments. These cases are indicated with an asterisk (*). The names represent only the basic nucleus -- the degree of alkyl substitution is determined by examining ELCOMP. Thus, a $C_8H_{10}O$ methoxy benzene is actually a methyl methoxy benzene. A $C_9H_{10}O$ benzaldehyde is a dimethyl benzaldehyde, etc.

An additional discussion of the significance of the structure assignments is given in Appendix G.

TABLE F-1

Mass Spectrometry - Odor Data - Sample 51C-34/5

Peak 7,8 -- APE 0.8 to 0.9 -- OV 128° -- SP 70°/4° (8%)

Sweet, fragrant, particle size, smoky

%	EXP	SPT	Odor	MW(R+DB)	ELCOMP	Structure Type
0.1	1.5	126		126(2)	$C_8H_{14}O$	Cyclohexanone
0.2	2.0	128		134(4)	$C_{10}H_{14}$	t-butyl benzene*
0.1	2.5	132		100(2)	$C_5H_8O_2$	4-hydroxy-2-pentenone*
0.3	4.0	135		142(2)	$C_8H_{14}O$	Hydroxyalkenone
0.6	5.0	137		110(3)	$C_7H_{10}O$ }	Furans
				124(3)	$C_8H_{12}O$	
0.4	5.5	139		120(5)	C_8H_8O	Acetophenone
0.4	6.0	140		138(4)	$C_8H_{10}O_2$	1,2-dimethoxy benzene*
0.4	6.5	141		124(4)	$C_7H_8O_2$	Furan
0.8	7.5	144		124(4)	$C_7H_8O_2$	Furan
0.2	8.0	147		112(3)	$C_6H_8O_2$	MCP*
				122(4)	$C_8H_{10}O$	Furan
1.3	8.5	149		110(4)	$C_6H_6O_2$	Methyl furfural
0.6	9.0	159		108(4)	C_7H_8O	o-Cresol*
1.0	9.5	165		108(4)	C_7H_8O	m-Cresol*

Peak 9 -- APE 0.95 to 1.05 -- OV 138° -- SP 70°/4° (6%)

Smoky, linseed

%	EXP	SPT	Odor	MW	ELCOMP	Structure Type
0.2	7.0	138	Oxidized oil, chalky	124(3)	$C_8H_{12}O$	Dimethyl cyclohexenone*
0.3	7.5	140	Sour, leathery	96(3)	C_6H_8O	Dimethyl furan
0.6	8.0	142	Burnt oil	100(2)	$C_5H_8O_2$	Valerolactone
0.6	8.5	143	Linseed oil	114(1)	$C_7H_{14}O$	Heptanone
0.1	10.0	150	Leathery	126(3)	$C_7H_{10}O_2$	Methyl cyclohexanedione
0.1	11.0	155	Irritation	96(3)	C_6H_8O	Furan
1.0	11.5	158	Woody	122(4)	$C_8H_{10}O$	2,6 dimethyl phenol*

Table F-1 continued.........

Peak 10 -- APE 1.2 to 1.3 -- OV 144° -- SP 70°/4° (5%)

Smoky

%	Exp	SPT	Odor	MW(R+DB)	ELCOMP	Structure Type
0.3	2.5	143	Smoky	136(4) 152(4)	$C_9H_{12}O$ $C_9H_{12}O_2$	Methoxy benzene Dimethoxy benzene
0.4	3.0	144	Smoky	134(5)	$C_9H_{10}O$	Dimethyl benzaldehyde*
0.5	4.0	147	Pungent	146(6)	$C_{10}H_{10}O$	Benzofuran
0.2	4.5	150	Sour	132(6)	C_9H_8O	2-indanone*

Peak 11 -- APE 1.35 to 1.45 -- OV 152° -- SP 70°/4° (3%)

Gassy, particle size

0.4	5.5	155	Oxidized oil	220(4)	$C_{15}H_{24}O$	Methoxy benzene
0.2	8.5	170	Burnt phenolic	134(6)	$C_8H_6O_2$	3-coumaranone

Peak 13 -- APE 1.5 to 1.6 -- OV 158° -- SP 70°/4° (6%)

Leathery, sour, pungent

0.3	8.5	147	Oxidized oil	152(3)	$C_{10}H_{16}O$	Dienone
1.0	11.0	162	Burnt, smoky	132(6)	C_9H_8O	1-indanone*
0.3	11.5	170	Burnt, smoky	136(5)	$C_8H_8O_2$	Hydroxy acetophenone*
0.3	12.0	179	Pungent, burnt smoky	136(4)	$C_9H_{12}O$	Trimethyl phenol*

Peak 14 -- APE 1.6 to 1.75 -- OV 162° -- SP 100°/4° (6%)

Smoky, pungent

0.4	2.0	142	Chalky	120(5)	C_8H_8O	Benzaldehyde
0.4	5.0	165	Pungent, garlic	132(6)	C_9H_8O	Indanone*

Peak 15 -- APE 1.75 to 1.8 -- OV 165° -- SP 100°/4° (2%)

Smoky, pungent

0.1	3.5	161	Metallic	148(5)	$C_{10}H_{12}O$	Benzaldehyde
0.2	4.0	162	Smoky, tarry	160(6)	$C_{11}H_{12}O$	Dimethyl-1-indanone*
0.2	4.5	165	Pungent, garlic	146(6)	$C_{10}H_{10}O$	1-tetralone*

TABLE F-2

Mass Spectrometry - Odor Data - Sample 52C-34/5/6 plus 56C-39/40

Peak 9 -- APE 1.0 to 1.1 -- OV 116° -- SP 100°/2° (5%)

Oily, woody, burnt, rubbery, particle size

%	EXP	SPT	Odor	MW(R+DB)	ELCOMP	Structure Type
0.3	2.0	135	Smoky, irritation	124(3)	$C_8H_{12}O$	Dimethyl cyclohexenone*
0.3	2.5	137	Phenolic	122(4)	$C_8H_{10}O$	Methylmethoxy benzene*
0.4	3.0	139	Oily linseed, pungent	142(2)	$C_8H_{14}O_2$	Hydroxy alkenone
0.5	3.5	140	Green, sour, burnt	140(3)	$C_8H_{12}O_2$	Oxy furan
				138(4)	$C_8H_{10}O_2$	Dimethoxy benzene*
0.4	4.0	141	Fragrant	134(5)	$C_9H_{10}O$	Dimethyl benzaldehyde*
0.2	4.5	146	Pungent, burnt	124(4)	$C_7H_8O_2$	Furan aldehyde
0.3	6.0	151	Musty, burnt	110(4)	$C_6H_6O_2$	Dihydroxy benzene
0.5	6.5	153	Sooty	110(4)	$C_6H_6O_2$	Dihydroxy benzene
1.3	7.0	164	Burnt, pungent, garlic	108(4)	C_7H_8O	m-Cresol*

Table F-2 cont.........

Peak 10 -- APE 1.1 to 1.2 -- OV 120° -- SP 100°/2° (2%)

Phenolic, pungent, linseed, woody, smoky

%	EXP	SPT	Odor	MW(R+DB)	ELCOMP	Structure Type
0.1	2.0	138	Fragrant	136(4)	$C_9H_{12}O$	Dimethyl anisole*
			Pungent	138(3)	$C_9H_{14}O$	Furan
0.1	2.5	140	Pungent	134(5)	$C_9H_{10}O$	Dimethyl benzaldehyde*
				96(3)	C_6H_8O	Dimethyl furan*
0.1	3.0	141	Fruity	138(4)	$C_8H_{10}O_2$	Dimethoxy benzene*
0.2	3.5	142	Burnt wax	134(5)	$C_9H_{10}O$	Dimethyl benzaldehyde*
0.2	4.0	142	Pungent	134(5)	$C_9H_{10}O$	Dimethyl benzaldehyde*
0.1	4.5	143	Pungent, sour	138(4)	$C_8H_{10}O_2$	Dimethoxy benzene*
0.2	5.0	144	Oily, spicy	124(4)	$C_7H_8O_2$	Furan aldehyde
0.1	5.5	148	Metallic	136(5)	$C_8H_8O_2$	Hydroxy acetophenone*
0.1	6.0	149	Linseed oil	136(5)	$C_8H_8O_2$	Isomer
0.3	6.5	153	Smoky, phenolic	122(4)	$C_8H_{10}O$	Dimethyl phenol*
				120(5)	C_8H_8O	Acetophenone
0.1	7.0	155	Sour	138(5)	$C_7H_6O_3$	?

Table F-2 cont.........

Peak 11 -- APE 1.2 to 1.4 -- OV 126° -- SP 100°/2° (8%)

Oily, particle size, smoky

%	EXP	SPT	Odor	MW(R&DB)	ELCOMP	Structure Type
0.5	7.5	145	Oily, sour	114(2)	$C_6H_{10}O_2$	Hydroxy alkenone
0.5	8.0	141	Particle size	134(5)	$C_9H_{10}O$	Dimethyl benzaldehyde*
0.3	9.0	156	Pungent, metallic	124(4)	$C_7H_8O_2$	Methoxy phenol*
0.3	9.5	160	Particle size, spicy	134(6)	$C_8H_6O_2$	Oxy benzofuran
0.2	10.0	167	Smoky rubber	122(5)	$C_7H_6O_2$	?
1.2	10.5	172	Particle size, pungent	122(4)	$C_8H_{10}O$	Xylenol*

Peak 12 -- APE 1.4 to 1.5 -- OV 134° -- SP 100°/2° (5%)

Burnt oily, burnt rubber, pungent

0.2	1.5	149	Musty	148(5)	$C_{10}H_{12}O$	Dimethyl acetophenone*
				156(2)	$C_9H_{16}O_2$	Hydroxy alkenone
0.4	2.0	150	Burnt oil	138(3)	$C_9H_{14}O$	Furan
				152(4)	$C_9H_{12}O_2$	Dimethoxy benzene
0.2	3.0	160	Tarry	138(4)	$C_8H_{10}O_2$	Methylmethoxy phenol*
0.2	4.0	164	Particle size, metallic	134(5)	$C_9H_{10}O$	Indanol*
				152(5)	$C_8H_8O_3$	Dihydroxy acetophenone*
0.2	4.5	166	Burnt sweet	136(4)	$C_9H_{12}O$	Benzyl alcohol
				134(5)	$C_9H_{10}O$	Allyl phenol*
0.3	5.0	168	Chalky, particle size	134(6)	$C_8H_6O_2$	2-coumaranone*
0.9	5.5	169	Linseed oil, pungent	134(6)	$C_8H_6O_2$	Hydroxy benzofuran
0.2	6.0	175	Irritation	122(4)	$C_8H_{10}O$	Xylenol*

Table F-2 cont.......

Peak 13 -- APE 1.5 to 1.7 -- OV 140° -- SP 100°/2° (8%)

Musty, green, metallic, smoky

%	EXP	SPT	Odor	MW(R&DB)	ELCOMP	Structure Type
0.2	1.5	148	Oily, naphthanate	148(5)	$C_{10}H_{12}O$	Anethole*
				150(4)	$C_{10}H_{14}O$	Methoxy benzene
0.3	2.0	149	Sour, particle size	160(6)	$C_{11}H_{12}O$	Indanone
0.3	3.5	155	Metallic, linseed oil	146(6)	$C_{10}H_{10}O$	Indanone
0.2	4.0	158	Burnt rubber	138(4)	$C_8H_{10}O_2$	Methylmethoxy phenol*
1.9	4.5	160	Irritation	132(6)	C_9H_8O	Indanone*
0.3	5.0	161	Sweet, chalky	132(6)	C_9H_8O	Cinnamaldehyde*
0.2	5.5	167	Sweet spicy	134(5)	$C_9H_{10}O$	Allyl phenol*
				148(6)	$C_9H_8O_2$	Hydroxy benzofuran
0.2	6.0	169	Green, fragrant	146(7)	$C_9H_6O_2$	Hydroxy Indenone
0.2	6.5	174	Linseed oil, naphthanate	132(6)	C_9H_8O	Indenol
0.2	7.0	177	Irritation	136(4)	$C_9H_{12}O$	Trimethyl phenol*
				136(6)	$C_7H_4O_3$	?

Table F-2 cont.......

Peak 14 -- APE 1.7 to 1.8 -- OV 145° -- SP 100°/2° (5%)

Sweet, oily, burnt

%	EXP	SPT	Odor	MW(R+DB)	ELCOMP	Structure Type
0.4	8.5	156	Smoky exhaust	180(4)	$C_{11}H_{16}O_2$	Dimethoxy benzene
				168(3)	$C_{10}H_{16}O_2$	Hydroxy furan
				164(4)	$C_{11}H_{16}O$	Methoxy benzene
				148(5)	$C_{10}H_{12}O$	Benzaldehyde
0.3	9.0	158	Sour, metallic	160(6)	$C_{11}H_{12}O$	Indanone
0.3	9.5	160	Sour, oily	168(3)	$C_{10}H_{16}O_2$	Hydroxy furan
				146(6)	$C_{10}H_{10}O$	Indanone
0.2	10.0	167	Painty	166(4)	$C_{10}H_{14}O_2$	Methoxy phenol
				144(7)	$C_{10}H_8O$	Indenone
0.2	10.5	171	Metallic, linseed oil	146(7)	$C_9H_6O_2$	Hydroxy indenone
0.2	11.5	176	Oily, metallic	148(6)	$C_9H_8O_2$	Hydroxy indanone
				150(5)	$C_9H_{10}O_2$	Methoxy benzaldehyde
0.4	12.0	178	Sour, oily	150(6)	$C_8H_6O_3$	Piperonal*
0.2	12.5	180	Smoky	152(5)	$C_8H_8O_3$	Piperonyl alcohol*
0.1	13.0	181	Smoky fat	150(4)	$C_{10}H_{14}O$	Tetramethyl phenol*
0.4	13.5	185	Asphyxiating, sweet	134(6)	$C_8H_6O_2$	Phthaldehyde*

Table F-2 cont..........

Peak 15 -- APE 1.8 to 1.9 -- OV 150° -- SP 120°/2° (5%)

Smoky, oily, irritation

%	EXP	SPT	Odor	MW(R+DB)	ELCOMP	Structure Type
0.1	10.5	154	Burnt metal	178(4)	$C_{12}H_{18}O$	Methoxy benzene
0.2	11.0	155	Chalky	180(4)	$C_{11}H_{16}O_2$	Dimethoxy benzene
0.2	11.5	158	Smoky, metallic	174(6)	$C_{12}H_{14}O$	Indanone*
0.2	12.5	169	Smoky fat	146(6)	$C_{10}H_{10}O$	Indanone
0.2	13.0	170	Irritation	164(5)	$C_{10}H_{12}O_2$	Hydroxy benzaldehyde
				162(6)	$C_{10}H_{10}O_2$	Hydroxy indanone
0.3	14.0	182	Soft coal smoke	148(6)	$C_9H_8O_2$	Hydroxy indanone
0.5	14.5	183	Smoky	148(6)	$C_9H_8O_2$	Hydroxy indanone

Peak 16/17 -- APE 1.85 to 2.05 --OV 158° -- SP 120°/2° (8%)

Smoky, sweet, waxy

%	EXP	SPT	Odor	MW(R&DB)	ELCOMP	Structure Type
0.2	2.5	144	Burnt sweet, pungent	134(5)	$C_9H_{10}O$	Benzaldehyde
0.6	8.0	184	Smoky	162(6)	$C_{10}H_{10}O_2$	Hydroxy indanone
0.9	9.0	190	Leathery, sour	162(6)	$C_{10}H_{10}O_2$	Hydroxy indanone
				160(7)	$C_{10}H_8O_2$	Hydroxy indenone
0.4	9.5	192	Smoky	156(8)	$C_{11}H_8O$	Naphthaldehyde

TABLE F-3

Mass Spectrometry - Odor Data -- Sample 60C-39/40/41

Peak 18/19/20 -- APE 1.95 to 2.15 -- OV 166° -- SP 120°/2° (9%)

Smoky, burnt, metallic, oily

%	EXP	SPT	Odor	MW(R&DB)	ELCOMP	Structure Type
0.3	3.5	188	Smoky	162(6)	$C_{10}H_{10}O_2$	Hydroxy indanone
				156(8)	$C_{11}H_8O$	Napthaldehyde
0.6	4.0	192	Oxidized oil	176(6)	$C_{11}H_{12}O_2$	Hydroxy indanone
0.1	4.5	194	Burnt tarry	148(6)	$C_9H_8O_2$	Hydroxy indanone
				134(5)	$C_9H_{10}O$	Indanol
0.3	5.0	200	Burnt rubber	162(6)	$C_{10}H_{10}O_2$	Hydroxy indanone
				160(7)	$C_{10}H_8O_2$	Hydroxy indenone

Peak 21/22 -- APE 2.15 to 2.30 -- OV 182° -- SP 120°/2° (6%)

Smoky, burnt oil

0.3	9.0	190	smoky oil	148(6)	$C_9H_8O_2$	Hydroxy indanone
				146(7)	$C_9H_6O_2$	Hydroxy indenone
0.3	9.5	191	smoky metallic	160(7)	$C_{10}H_8O_2$	Hydroxy indenone
0.5	10.0	193	pungent, oxidized	162(6)	$C_{10}H_{10}O_2$	Hydroxy indanone
				148(6)	$C_9H_8O_2$	Hydroxy indanone
0.3	11.0	202	smoky, oily	160(7)	$C_{10}H_8O_2$	Hydroxy indenone

TABLE F-4

Mass Spectrometry - Odor Data - Sample 56P-40

Peak 10/11a -- APE 1.1 to 1.3 -- OV 124° -- SP 100°/2° (6%)

Oxidized Oil, linseed

%	EXP	SPT	Odor	MW(R+DB)	ELCOMP	Structure Type
0.2	7.0	129	Metallic, pungent	180(3)	$C_{12}H_{20}O$	Dienone
				166(3)	$C_{11}H_{18}O$	Dienone
				168(2)	$C_{11}H_{20}O$	Alkenone
0.2	8.0	134	Oxidized oil, aldehydic	154(2)	$C_{10}H_{18}O$	Alkenone
				152(3)	$C_{10}H_{16}O$	Dienone
0.2	8.5	138	Burnt sweet	150(4)	$C_{10}H_{14}O$	Methoxy benzene
				148(5)	$C_{10}H_{12}O$	Benzaldehyde
				138(3)	$C_9H_{14}O$	Furan
				136(4)	$C_9H_{12}O$	Methoxy benzene
0.4	9.0	140	Linseed, irritation	134(5)	$C_9H_{10}O$	Dimethyl benzaldehyde*
0.6	9.5	142	Oily aldehydic	148(5)	$C_{10}H_{12}O$	Dimethyl acetophenone*
				134(5)	$C_9H_{10}O$	Dimethyl benzaldehyde*
0.6	10.0	143	Fruity	148(5)	$C_{10}H_{12}O$	Benzaldehyde
0.3	10.5	144	Pungent	134(5)	$C_9H_{10}O$	Dimethyl benzaldehyde*
0.2	11.0	145	Burnt woody	134(5)	$C_9H_{10}O$	Benzaldehyde
0.6	11.5	146	Pungent, sour	148(5)	$C_{10}H_{12}O$	Dimethyl acetophenone*
				136(5)	$C_8H_8O_2$	Hydroxy acetophenone*
0.4	12.0	147	Oxidized oil, fragrant	132(6)	C_9H_8O	Phenyl vinyl ketone
0.2	12.5	149	Irritation	136(5)	$C_8H_8O_2$	Hydroxy acetophenone
				150(5)	$C_9H_{10}O_2$	Methoxy benzaldehyde*
0.3	13.0	150	Burnt sweet	130(7)	C_9H_6O	Indenone

Table F-4 cont.............

Peak 11b, 11c & 12 -- APE 1.3 to 1.5 -- OV 130° -- SP 100°/2° (6%)

Pungent, oily, burnt

%	EXP	SPT	Odor	MW(R+DB)	ELCOMP	Structure Type
0.3	3.0	133	Fragrant	166(3)	$C_{11}H_{18}O$	Dienone
				162(4)	$C_{12}H_{18}$	Alkyl benzene
0.3	4.5	145	Pungent, spicy	148(5)	$C_{10}H_{12}O$	Dimethyl acetophenone*
				150(4)	$C_{10}H_{14}O$	Methoxy benzene
0.4	5.0	147	Sour, leathery	148(5)	$C_{10}H_{12}O$	Anethole*
0.3	5.5	149	Sour dish rag	150(4)	$C_{10}H_{14}O$	Methoxy benzene
0.2	6.0	153	Solvent, linseed	148(5)	$C_{10}H_{12}O$	Benzaldehyde
0.2	6.5	159	Naphthenate	144(7)	$C_{10}H_8O$	Indenone
				150(5)	$C_9H_{10}O_2$	Methoxy benzaldehyde
0.1	7.0	160	Chalky, spicy	132(6)	C_9H_8O	1-indanone
0.1	7.5	167	Sour naphthenate	132(6)	C_9H_8O	Indenol

Peak 13 -- APE 1.5 to 1.65 -- OV 140° -- SP 100°/2° (8%)

Pungent, oxidized oil, smoky fat

2.0	5.0	150	Burnt fat	162(5)	$C_{11}H_{14}O$	Benzaldehyde
				148(5)	$C_{10}H_{12}O$	Benzaldehyde

Peak 14 -- APE 1.65 to 1.75 -- OV 145° -- SP 100°/2° (7%)

Oxidized oil, aldehyde

0.6	9.0	149	Aldehydic	194(3)	$C_{13}H_{22}O$	Dienone
				180(3)	$C_{12}H_{20}O$	Dienone
0.4	9.5	161	Oily	148(5)	$C_{10}H_{12}O$	Benzaldehyde
				162(5)	$C_{11}H_{14}O$	Benzaldehyde

Table F-4 cont........

Peak 15, 16, 17 -- APE 1.75 to 2.0 -- OV 152° -- SP 120°/2° (16%)

Smoky, linseed, burnt fat

%	EXP	SPT	Odor	MW(R+DB)	ELCOMP	Structure Type
1.1	1.5	141	Sour	194(3)	$C_{13}H_{22}O$	Dienone
				190(4)	$C_{14}H_{22}$	Alkyl benzene
				180(2)	$C_{13}H_{14}$	Diene
1.1	2.0	158	Oxidized oil, tarry, pungent	190(5)	$C_{13}H_{18}O$	Benzaldehyde
				178(4)	$C_{12}H_{18}O$	Methoxy benzene
0.8	2.5	163	Metallic, burnt	160(6)	$C_{11}H_{12}O$	Indanone
0.5	3.0	167	Pungent, leathery	158(7)	$C_{11}H_{10}O$	Indenone
				160(6)	$C_{11}H_{12}O$	Methyl tetralone*

Peaks 18/19 -- APE 2.0 to 2.25 -- OV 162° -- SP 120°/2° (13%)

Burnt oil, pungent, green, smoky

0.3	6.5	185	Particle size, smoky	172(8)	$C_{11}H_{8}O_{2}$	Methyl naphthoquinone*
1.2	7.0	187	Woody, irritation	156(8)	$C_{11}H_{8}O$	1-Naphthal
0.1	7.5	192	Sour, leathery	160(7)	$C_{10}H_{8}O_{2}$	Hydroxy indenone
				162(6)	$C_{10}H_{10}O_{2}$	Hydroxy indanone

Peaks 20/21/22 -- APE 2.25 to 2.6 -- OV 175° -- SP 120°/2° (21%)

Burnt predominates

0.4	1.5	187	Smoky, burnt	204(6)	$C_{13}H_{16}O_{2}$	Hydroxy indanone
				200(7)	$C_{14}H_{16}O$	Indenone
0.4	2.0	192	Irritation, smoky	190(6)	$C_{12}H_{14}O_{2}$	Hydroxy indanone
				186(8)	$C_{12}H_{10}O_{2}$	Methoxy naphthaldehyde
0.8	2.5	194	Smoky	170(8)	$C_{12}H_{10}O$	Acetonaphthone*
1.7	3.0	196	Pungent, sour, oily	170(8)	$C_{12}H_{10}O$	Naphthaldehyde
1.3	3.5	198	Smoky, particle size	170(8)	$C_{12}H_{10}O$	Acetonaphthone*
				174(7)	$C_{11}H_{10}O_{2}$	Hydroxy indenone
0.1	4.0	204	Pungent, smoky	176(6)	$C_{11}H_{12}O_{2}$	Methoxy tetralone*

APPENDIX G

Smoky-Burnt Structure Data Organized by R+DB Values

Attempts to find suitable means of assembling a summary of the observed data have been frustrated by the great degree of overlap observed in structure-odor relationships. These attempts are further confused by the presence of several functional groups on the same nucleus. The one means which we have found convenient is to list the observed data according to the compositionally defined R+DB values. In this way, any subsequent revisions of specific structure assignments would not require complete rearrangement of the data. All of the data are summarized in this manner in Table G-1.

The data in the table are arranged in order of increasing R+DB value. The possible hypothetical structure for given combinations of oxygen from Appendix E are also included for referencing convenience. The data obtained from the chloroform and pentane extract samples are separated by the double line (═).

In examining the chemical data in Table G-1 and observing the repetition of certain species, it might at first seem that a single species from the exhaust has been reported several times. The data in the table has actually been assembled with care taken to eliminate duplication of species from Appendix F which did have the same GC retention times in either the chloroform or pentane extracts. It is our present interpretation that nearly each of the species listed represents a unique isomer of a given molecular formula. There is, however, some duplication in reporting between the chloroform and pentane series.

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TABLE G-1

Individual Species Observed in the Smoky-Burnt Studies

R + DB CLASS 1

O_1 - ketones, aldehydes, cyclic-ols

MW	ELCOMP	Odor	Structure type
a 114	$C_7H_{14}O$	Linseed Oil	Heptanone

R + DB CLASS 2

O_1 - alkenones, cyclic carbonyls

O_2 - alkene or cyclic acids and esters, dicarbonyls
dicarbonyls, oxy cyclo carbonyl,
oxy alkenones

MW	ELCOMP	Odor	Structure Type
142	$C_8H_{14}O$	Linseed oil, pungent	Hydroxy alkenone
100	$C_5H_8O_2$	Burnt oil	Valerolactone
114	$C_6H_{10}O_2$	Oily sour	Hydroxy alkenone
a 156	$C_9H_{16}O_2$	Musty	Hydroxy alkenone
168	$C_{11}H_{20}O$	Metallic, Pungent	Alkenone
154	$C_{10}H_{18}O$	Oxidized oily, aldehydic	Alkenone

a. data above = observed in chloroform extracts
data below = observed in pentane extract

Table G-1 cont..........

R+DB CLASS 3

O_1 - Dienones, furans, cyclic-ene carbonyls

O_2 - MPS,s, cyclodiones, oxy furans

MW	ELCOMP	Odor	Structure Type
124	$C_8H_{12}O$	Irritation, smoky	Cyclohexenone
126	$C_7H_{10}O$	Leathery	Cyclohexanedione
140	$C_8H_{12}O_2$	Green, sour, burnt	Oxy furan
96	C_6H_8O	Sour, leathery	Furan
96	C_6H_8O	Irritation	Furan
152	$C_{10}H_{16}O$	Oxidized oil	Dienone
138	$C_9H_{14}O$	Pungent	Furan
168	$C_{10}H_{16}O_2$	Burnt oil	Hydroxy furan
168	$C_{10}H_{16}O_2$	Sour, oily	Hydroxy furan
180	$C_{12}H_{20}O$	Metallic, pungent	Dienone
166	$C_{11}H_{18}O$	Metallic, pungent	Dienone
152	$C_{10}H_{16}O$	Oxidized oily, aldehydic	Dienone
138	$C_9H_{14}O$	Burnt sweet	Furan
194	$C_{13}H_{22}O$	Aldehydic	Dienone
180	$C_{12}H_{20}O$	Aldehydic	Dienone

Table G-1 cont.......

R+DB CLASS 4

O_1 - Phenols, methoxy benzenes, benzyl alcohols

O_2 - Methoxy (hydroxy) phenols, furfurals

MW	ELCOMP	Odor	Structure Type
122	$C_8H_{10}O$	Woody	Dimethyl phenol
152	$C_9H_{12}O_2$	Smoky	Dimethoxy benzene
220	$C_{15}H_{24}O$	Oxidized oil	Methoxy benzene
136	$C_9H_{12}O$	Burnt smoky	Trimethyl phenol
122	$C_8H_{10}O$	Phenolic	Methoxy benzene
136	$C_9H_{12}O$	Smoky	Methoxy benzene
138	$C_8H_{10}O_2$	Burnt	Dimethoxy benzene
124	$C_7H_8O_2$	Burnt	Furan aldehyde
108	C_7H_8O	Burnt, pungent, garlic	m-Cresol
110	$C_6H_6O_2$	Burnt, musty	Dihydroxy benzene
110	$C_9H_6O_2$	Sooty	Dihydroxy benzene
136	$C_9H_{12}O$	Fragrant	Dimethyl anisole
138	$C_8H_{10}O_2$	Fruity	Dimethoxy benzene
183	$C_8H_{10}O_2$	Pungent, sour	Dimethoxy benzene
124	$C_7H_8O_2$	Oily, spicy	Furan aldehyde
122	$C_8H_{10}O$	Smoky, phenolic	Phenol
124	$C_7H_8O_2$	Pungent, metallic	Methoxy phenol
122	$C_8H_{10}O$	Particle size, pungent	Xylenol
136	$C_9H_{12}O$	Pungent, burnt	Phenol
152	$C_9H_{12}O_2$	Burnt oil	Dimethoxy benzene
138	$C_8H_{10}O_2$	Tarry	Methoxy phenol
122	$C_8H_{10}O$	Irritation	Xylenol
150	$C_{10}H_{14}O$	Oily, Naphthenate	Methoxy benzene
136	$C_9H_{12}O$	Irritation	Phenol
180	$C_{11}H_{16}O_2$	Smoky, exhaust	Dimethoxy benzene
164	$C_{11}H_{16}O$	Burnt oil	Methoxy benzene
166	$C_{10}H_{14}O_2$	Painty	Methoxy phenol
150	$C_{10}H_{14}O$	Smoky fat	Phenol
178	$C_{12}H_{18}O$	Burnt metal	Methoxy benzene
180	$C_{11}H_{16}O_2$	Chalky	Dimethoxy benzene
150	$C_{10}H_{14}O$	Burnt sweet	Methoxy benzene
150	$C_{10}H_{14}O$	Pungent, spicy	Methoxy benzene
136	$C_9H_{12}O$	Sharp	Methoxy benzene
150	$C_{19}H_{14}O$	Sour dish rag	Methoxy benzene
178	$C_{12}H_{18}O$	Tarry, pungent	Phenol

Table G-1 cont.......

R+DB CLASS 5

O_1 - Phenyl carbonyls, indanols, allyl phenols, dihydrobenzofuran

O_2 - Aromatic acids, hydroxy(methoxy) aromatic carbonyls, oxy indanols, allyl phenols, quinones

O_3 - Oxy benzoic acids, dioxy phenyl carbonyls, dioxy allyl phenols, oxy quinones

MW	ELCOMP	Odor	Structure Type
134	$C_9H_{10}O$	Smoky	Benzaldehyde
136	$C_8H_8O_2$	Burnt, smoky	Hydroxy acetophenone
120	C_8H_8O	Chalky	Benzaldehyde
134	$C_9H_{10}O$	Fragrant	Benzaldehyde
134	$C_9H_{10}O$	Pungent	Benzaldehyde
134	$C_9H_{10}O$	Burnt wax	Benzaldehyde
136	$C_8H_8O_2$	Metallic	Hydroxy acetophenone
136	$C_8H_8O_2$	Linseed Oil	Isomer
120	C_8H_8O	Smoky	Acetophenone
138	$C_7H_6O_3$	Sour	?
134	$C_9H_{10}O$	Particle size	Benzaldehyde
122	$C_7H_6O_2$	Smoky rubber	?
136	$C_8H_8O_2$	Burnt	Hydroxy benzaldehyde
148	$C_{10}H_{12}O$	Musty	Acetophenone
134	$C_9H_{10}O$	Particle size	Indanol
152	$C_8H_8O_3$	Metallic	Dihydroxy acetophenone
134	$C_9H_{10}O$	Burnt sweet	Allyl phenol
148	$C_{10}H_{12}O$	Oily, Naphthenate	Anethole
148	$C_{10}H_{12}O$	Smoky exhaust	Benzaldehyde
150	$C_9H_{10}O_2$	Oily, metallic	Methoxy benzaldehyde
152	$C_8H_8O_3$	Smoky	Piperonyl alcohol
164	$C_{10}H_{12}O_2$	Irritation	Hydroxy benzaldehyde
134	$C_9H_{10}O$	Burnt, sweet, pungent	Indanol
148	$C_{10}H_{12}O$	Burnt sweet	Benzaldehyde
134	$C_9H_{10}O$	Linseed, irritation	Benzaldehyde
148	$C_{10}H_{12}O$	Oily aldehydic	Acetophenone
148	$C_{10}H_{12}O$	Fruity	Benzaldehyde
134	$C_9H_{10}O$	Burnt woody	Benzaldehyde
148	$C_{10}H_{12}O$	Pungent, sour	Acetophenone
136	$C_8H_8O_2$	Pungent, sour	Hydroxy acetophenone
136	$C_8H_8O_2$	Irritation	Hydroxy acetophenone
150	$C_9H_{10}O_2$	Naphthenate	Methyoxy benzaldehyde
162	$C_{11}H_{14}O$	Burnt fat	Benzaldehyde
190	$C_{13}H_{18}O$	Oxidized oil	Benzaldehye

Table G-1 cont.......

R+DB CLASS 6

O_1 - benzofurans, indanones, indenols, phenyl-ene-carbonyls

O_2 - oxy benzofurans, oxy indanones, phenyl propene acids, dihydrocoumarins, aromatic dialdehydes

O_3 - dioxy allyl benzaldehydes

MW	ELCOMP	Odor	Structure Type[a]
146	$C_{10}H_{10}O$	Pungent	Benzofuran
132	C_9H_8O	Sour	Indanone
146	$C_{10}H_{10}O$	Pungent, garlic	Tetralone
134	$C_8H_6O_2$	Particle size, spicy	Oxy benzofuran
134	$C_8H_6O_2$	Chalky, particle size	Coumaranone
134	$C_8H_6O_2$	Linseed oil, pungent	Hydroxy benzofuran
160	$C_{11}H_{12}O$	Sour, particle size	Indanone
146	$C_{10}H_{10}O$	Metallic Linseed oil	Indanone
132	C_9H_8O	Irritation	Indanone
132	C_9H_8O	Sweet, chalky	Cinnamaldehyde
148	$C_9H_8O_2$	Sweet, spicy	Hydroxy benzofuran
132	C_9H_8O	Linseed oil, naphthenate	Indenol
136	$C_7H_4O_3$	Irritation	?
160	$C_{11}H_{12}O$	Sour, Metallic	Indanone
146	$C_{10}H_{10}O$	Sour, oily	Indanone
148	$C_9H_8O_2$	Oily, metallic	Hydroxy indanone
150	$C_8H_6O_3$	Sour, oily	Piperonal
134	$C_8H_6O_2$	Asphyxiating, sweet	Phthaldehyde
174	$C_{12}H_{14}O$	Smoky, metallic	Indanone
146	$C_{10}H_{10}O$	Smoky fat	Indanone
162	$C_{10}H_{10}O_2$	Irritation	Hydroxy indanone
148	$C_9H_8O_2$	Soft coal smoke	Hydroxy indanone
148	$C_9H_8O_2$	Smoky	Hydroxy indanone
162	$C_{10}H_{10}O_2$	Smoky	Hydroxy indanone
162	$C_{10}H_{10}O_2$	Sour	Hydroxy indanone
176	$C_{11}H_{12}O_2$	Oxidized oil	Hydroxy indanone
132	C_9H_8O	Oxidized oil, fragrant	Phenyl vinyl ketone
132	$C_9H_8O_2$	Chalky, spicy	Indanone
132	$C_9H_8O_2$	Sour naphthenate	Indenol
160	$C_{11}H_{12}O$	Metallic, burnt	Indanone
160	$C_{11}H_{12}O$	Pungent, leathery	Tetralone
162	$C_{10}H_{10}O_2$	Sour, leathery	Hydroxy indanone
204	$C_{13}H_{16}O_2$	Smoky	Hydroxy indanone
190	$C_{12}H_{14}O_2$	Smoky, irritation	Hydroxy indanone
176	$C_{11}H_{12}O_1$	Pungent, smoky	Methoxy tetralone

a. from C_{10} tetralones may also be considered as possible choices for indanones.

Table G-1 cont........

R+DB Class 7

O_1 - Naphthols, indenones

O_2 - Oxy naphthols, coumarins, oxy indenones

MW	ELCOMP	Odor	Structure Type
144	$C_{10}H_8O$	Painty	Indenone
146	$C_9H_6O_2$	Metallic, linseed oil	Hydroxy indenone
160	$C_{10}H_8O_2$	Leathery, sour	Hydroxy indenone
160	$C_{10}H_8O_2$	Burnt rubber	Hydroxy indenone
146	$C_9H_6O_2$	Smoky oil	Hydroxy indenone
160	$C_{10}H_8O_2$	Smoky metallic	Hydroxy indenone
130	C_9H_6O	Burnt sweet	Indenone
144	$C_{10}H_8O$	Naphthenate	Indenone
158	$C_{11}H_{10}O$	Pungent, leathery	Indenone
160	$C_{10}H_8O_2$	Sour, leathery	Hydroxy indenone
200	$C_{14}H_{16}O$	Smoky burnt	Indenone
174	$C_{11}H_{10}O_2$	Smoky, particle size	Hydroxy indenone

Table G-1 cont.......

R+D Class 8

O_1 - Naphthaldehydes

O_2 - Naphthoquinones, oxy naphthaldehydes

MW	ELCOMP	Odor	Structure Type
156	$C_{11}H_8O$	Smoky	Naphthaldehyde
172	$C_{11}H_8O_2$	Particle size, smoky	Naphthoquinone
156	$C_{11}H_8O$	Woody, irritation	Naphthaldehyde
186	$C_{12}H_{10}O_2$	Irritation, smoky	Methoxy naphthaldehyde
170	$C_{12}H_{10}O$	Smoky	Acetonaphthone
170	$C_{12}H_{10}O$	Smoky, particle size	Acetonaphthone

APPENDIX H

OXYGENATED REFERENCE COMPOUNDS

1. GAS CHROMATOGRAPHIC STUDIES

In an effort to confirm the chemical structure assignments and odor description associated with oxygenated compound classes related to diesel exhaust smoky-burnt odor, we have sought to obtain as many oxygenated reference compounds as appropriate based on the exhaust identification data and study their chromatographic behavior and odor characteristics. At the present time, 144 compounds have been studied, 33 of these have been identified in diesel exhaust. We will continue to study new materials as they come to our attention. Unfortunately, we have been unable to locate many of the compounds we wish to examine.

The GC retention data from the silicone OV-1 and Carbowax SP-1000 columns and the species fundamental molecular weight and elemental composition provide a precise basis for comparing data observed in the exhaust analysis. The data thus obtained for these materials is detailed in Table H-1. The compounds are listed in order of increasing elution from the silicone column. In obtaining the elution temperatures, primary elution standards were run with each material so that any changes in chromatographic behavior could be referenced to a common base. The data in the table are organized based on elution scales for each column. We have found it convenient to reference the silicone elution temperature to that of allyl phenyl ether, thus arriving at an APE value indicative of the relative elution behavior of each of the materials. The relationship between the silicone elution temperature, APE value, and exhaust sample peak numbers is shown in Figure E-2 of Appendix E. The data in Table H-1 are organized in order of increasing APE value and are listed to indicate that the compounds listed between adjacent APE values have retention times in that range. The Carbowax GC index is listed as an SPT (SP-1000 temperature) value and references all of the Carbowax retention temperatures to a common program rate of an initial 120°C and a 2°C/min heating rate.

These data have been compared to the smoky-burnt identification data reported in Appendix F. The requirement for a match used was that the two sets of GC data and elemental composition fit, as well as the requirement that the observed mass spectral fragmentation pattern be consistent with the structure. Species identified as being present in the exhaust samples

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have been indicated with an asterisk (*). The data has been useful both in confirming HRMS assignments or refining the isomeric details and also in eliminating such species as hydroxybenzoic acid and others which elute outside the regions studied.

2. TEST ROOM ODOR STUDIES

Many of the reference materials were examined for odor characteristics by study of the sample either directly in the bottle or on blotter strip. Several of these had sufficient odor intensity and the appropriate odor character to warrant quantitative study in the odor test room. The results of these studies are listed in Table H-2. Most of the studies were carried out with a solution (Soltrol 170 or methanol) injection of the material into the odor test room to give a concentration ranging from 0.1 - 12 $\mu g/m^3$.

Clearly many of the compounds studied have an odor character consistent with the assignments made in the exhaust samples. Of further significance, however, is that they also have an odor intensity comparable to the levels calculated to be present in the exhaust samples studied in the test room.

Table H-1

Gas Chromatographic Data on Oxygenated Reference Standards

APE[a]	Compound	MW	ELCOMP	R&DB	SPT
0.20					
	2,5 dimethylfuran	96	C_6H_8O	3	138
0.30					
	2,4 pentanedione	100	$C_5H_8O_2$	2	127
0.50					
	4-benzoquinone	108	$C_6H_4O_2$	5	132
	cyclohexanol	100	$C_8H_{12}O$	1	128
	2-furylmethyl ketone	110	$C_6H_6O_2$	4	131
	camphor	152	$C_{10}H_{16}O$	3	126
	γ-valerolactone	100	$C_5H_8O_2$	2	137
	* 4-hydroxy-2-pentenone	100	$C_5H_8O_2$	2	130.5
0.60					
	5-methyl-2-furaldehyde	110	$C_6H_6O_2$	4	134.5
	benzaldehyde	106	C_7H_6O	5	132
	phenol	94	C_6H_6O	4	158
0.70					
	3,4 & 3,5-cyclopentanediol	102	$C_5H_{10}O_2$	1	163.5
	2-cyclohexene-1-one	96	C_6H_8O	3	130
	2-methylanisole	122	$C_8H_{10}O$	4	128
0.8					
	* 1-methyl-cyclopentene-2-ol-3-one	112	$C_6H_8O_2$	3	146
	2,3-benzofuran	118	C_8H_6O	6	131
	1,4-cyclohexanedione	112	$C_6H_8O_2$	3	153
	4-methylanisole	122	$C_8H_{10}O$	4	131
	* phenylacetaldehyde	120	C_8H_8O	5	138
	acetophenone	120	C_8H_8O	5	138

a. Retention on OV-1 relative to allyl phenyl ether.

APE	Compound	MW	ELCOMP	R&DB	SPT
0.90					
	* o-cresol	108	C_7H_8O	4	157
	salicylaldehyde	122	$C_7H_6O_2$	5	140
	3-methylbenzaldehyde	120	C_8H_8O	5	137
	benzyl alcohol	108	C_7H_8O	4	148
	2,5-dimethyl-3-hexyne-2,5-diol	142	$C_8H_{14}O_2$	2	146
	* m-cresol	108	C_7H_8O	4	164
	p-cresol	108	C_7H_8O	4	162.5
1.00					
	allylphenyl ether (elution standard)	134	$C_9H_{10}O$	5	133
	2,6-dimethylanisole	136	$C_9H_{12}O$	4	130
	* 3,5-dimethyl-2-cyclohexene-1-one	124	$C_8H_{12}O$	3	137
	* 2,6-dimethylphenol	122	$C_8H_{10}O$	4	156
	2-furanacrolein	122	$C_7H_6O_2$	4	148.5
1.10					
	* 1,2-dimethyoxybenzene	138	$C_8H_{10}O_2$	4	141
	2-methylbenzyl alcohol	122	$C_8H_{10}O$	4	159
	4-methylbenzyl alcohol	122	$C_8H_{10}O$	4	157
	2,5-dimethyl phenol	122	$C_8H_{10}O$	4	164
1.20					
	1,3-dimethoxybenzene	138	$C_8H_{10}O_2$	4	143
	* 4-methylsalicylaldehyde	136	$C_8H_8O_2$	5	145
	5,5-dimethyl-1,3-cyclohexanedione	140	$C_8H_{12}O_2$	3	168
	2,4-xylenol	122	$C_8H_{10}O$	4	163
	* 3,5-dimethylphenol	122	$C_8H_{10}O$	4	172
	* 2,5-dimethylbenzaldehyde	134	$C_9H_{10}O$	5	143.5
	2-methyl-1,3-cyclohexanedione	126	$C_7H_{10}O_2$	3	179
	4-methoxyphenol	124	$C_7H_8O_2$	4	186'
	1-phenyl-1,2-propanedione	148	$C_9H_8O_2$	6	146
	2-methylbenzoic acid	136	$C_8H_8O_2$	5	194
	* 2,4-dimethylbenzaldehyde	134	$C_9H_{10}O$	5	144

APE	Compound	MW	ELCOMP	R&DB	SPT
1.30					
	4(2-furyl)-3-butene-2-one	136	$C_8H_8O_2$	5	162
	* 2-methoxy-4-methylphenol	138	$C_8H_{10}O_2$	4	155
	* 2-hydroxyacetophenone	136	$C_8H_8O_2$	5	147
	3,4-dimethylbenzaldehyde	134	$C_9H_{10}O$	5	148
	3-methoxyphenol	124	$C_7H_8O_2$	4	191.5
	* 3,4-xylenol	122	$C_8H_{10}O$	4	172.5
1.40					
	* 2-allylphenol	134	$C_9H_{10}O$	5	168
	1-(2-furyl)-1,3-butanedione	152	$C_8H_8O_3$	5	160
	3,4-dihydro-1-(2H)-naphthalenone	144	$C_{10}H_8O$	7	165.5
	2-methoxybenzaldehyde	136	$C_8H_8O_2$	5	157.5
	* 2,4-dimethylacetophenone	148	$C_{10}H_{12}O$	5	147
	3-methoxybenzaldehyde	136	$C_8H_8O_2$	5	153.5
	5-methylfurfuryl alcohol	112	$C_6H_8O_2$	3	143
	* cinnamaldehyde	132	C_9H_8O	6	160.5
	* 2-indanone	132	C_9H_8O	6	154
	* 2-coumaranone	134	$C_8H_6O_2$	6	164
1.50					
	* 1-indanone	132	C_9H_8O	6	160
	3,3,4,7-tetramethyl-1-indanone	188	$C_{13}H_{16}O$	6	163.5
	3-hydroxybenzaldehyde	122	$C_7H_6O_2$	5	213
	* α-hydroxyacetophenone	136	$C_8H_8O_2$	5	170
	2-hydroxy-3-methoxybenzaldehyde	152	$C_8H_8O_3$	5	173
1.60					
	1,3-indandione	146	$C_9H_6O_2$	7	182
	5-indanol	134	$C_9H_{10}O$	5	190
	2,6-dimethoxyphenol	154	$C_8H_{10}O_3$	4	178
	* 2,3,5-trimethylphenol	136	$C_9H_{12}O$	4	173.5
	cinnamic alcohol	134	$C_9H_{10}O$	5	178
	1,4-cyclohexanedimethanol	144	$C_8H_{16}O_2$	1	190

APE	Compound	MW	ELCOMP	R&DB	SPT
1.70					
	* Anethole	148	$C_{10}H_{12}O$	5	148
	4-methoxyacetophenone	150	$C_9H_{10}O_2$	5	169
	2-methyl-5-isopropylphenol	150	$C_{10}H_{14}O$	4	172
	2-hydroxybenzoic acid	138	$C_7H_6O_3$	5	(b)
	2-hydroxybenzyl alcohol	124	$C_7H_8O_2$	4	155
	* piperonyl alcohol	152	$C_8H_8O_3$	5	176
	2,3-dimethoxybenzaldehyde	166	$C_9H_{10}O_3$	5	171
	3,3,7-trimethyl-1-indanone	174	$C_{12}H_{14}O$	6	159
1.80					
	2,3-dimethoxybenzyl alcohol	168	$C_9H_{12}O_3$	4	187
	3-methoxybenzoic acid	152	$C_8H_8O_3$	5	217
	2,3,5,6-tetramethylphenol	150	$C_{10}H_{14}O$	4	171
	coumarin	146	$C_9H_6O_2$	7	190
	4-hydroxybenzaldehyde	122	$C_7H_6O_2$	5	220 + 2.2 min
	o-anisaldehyde	136	$C_8H_8O_2$	5	156
	* 2-methyl-1-tetralone	160	$C_{11}H_{12}O$	6	166
	5-methyl-2-hydroxybenzoic acid	152	$C_8H_8O_3$	5	220 + 33 min.
	* 3,3,5-trimethyl-1-indanone	174	$C_{12}H_{14}O$	6	159
	3,4-dimethoxybenzaldehyde	166	$C_9H_{10}O_3$	5	189
	1,2-cyclodecanedione	168	$C_{10}H_{16}O_2$	3	143
1.90					
	5,7-dimethyl-1-indanone	160	$C_{11}H_{12}O$	6	174
	3-methoxy-4-hydroxyacetophenone	166	$C_9H_{10}O_3$	5	204
	4,7-dimethyl-1-indanone	160	$C_{11}H_{12}O$	6	175.5
	p-(1,1-dimethylpropyl)phenol	164	$C_{11}H_{16}O$	4	187
	2,3,5,6-tetramethylacetophenone	176	$C_{12}H_{16}O$	5	165
	* 1-tetralone	146	$C_{10}H_{10}O$	6	166

APE	Compound	MW	ELCOMP	R&DB	SPT
2.00					
	coumarin	146	$C_9H_6O_2$	7	190
	* piperonal	150	$C_8H_6O_3$	6	175
	2-hydroxy-3-methylbenzoic acid	152	$C_8H_8O_3$	5	(b)
	3,5-dimethoxybenzyl alcohol	168	$C_9H_{12}O_3$	4	209
	4-hydroxyacetophenone	136	$C_8H_8O_2$	5	220 + 5 min.
	2-hydroxy-4-methoxyacetophenone	166	$C_9H_{10}O_3$	5	179
	5-acetylindan	160	$C_{11}H_{12}O$	6	174
	2,4-dimethoxybenzaldehyde	166	$C_9H_{10}O_3$	5	195
	2,4-dihydroxybenzaldehyde	138	$C_7H_6O_3$	5	220 + 12 min.
	3,3,5,6-tetramethyl-1-indanone	188	$C_{13}H_{16}O$	6	179
	3,3,4,6-tetramethyl-1-indanone	188	$C_{13}H_{16}O$	6	169
	3,3,5,7-tetramethyl-1-indanone	188	$C_{13}H_{16}O$	6	166
2.10					
	2,6-dihydroxyacetophenone	152	$C_8H_8O_3$	5	220 + 11 min.
	1-naphthol	144	$C_{10}H_8O$	7	220 + 1 min.
	2-methoxybenzoic acid	152	$C_8H_8O_3$	5	212
	2,3-dimethylbenzoic acid	150	$C_9H_{10}O_2$	5	206
	5,6,7,8-tetrahydronaphthol	148	$C_{10}H_{12}O$	5	202
2.20					
	2,4-dihydroxyacetophenone	152	$C_8H_8O_3$	5	(a)
	3,4-dimethoxyacetophenone	180	$C_{10}H_{12}O_3$	5	194
	2,5,8-trimethyl-1-tetralone	188	$C_{13}H_{16}O$	6	181
	3,5,8-trimethyl-1-tetralone	188	$C_{13}H_{16}O$	6	182
	3,3,6,8-tetramethyl-1-tetralone	202	$C_{14}H_{18}O$	6	175

APE	Compound	MW	ELCOMP	R&DB	SPT
2.30	* 1-acetonaphthone	170	$C_{12}H_{10}O$	8	192
	1,2,3,4-tetrahydro-2,5,8-trimethyl-1-naphthol	190	$C_{13}H_{18}O$	5	193
	4,5,7-trimethyl-1-indanone	174	$C_{12}H_{14}O$	6	191
	4,6,7-trimethyl-1 indanone	174	$C_{12}H_{14}O$	6	191
	5-methoxy-1-tetralone	176	$C_{11}H_{12}O_2$	6	196.5
	5,7-dimethyl-1-tetralone	174	$C_{12}H_{14}O$	6	190
	* 2-methyl-1,4-naphthaquinone	172	$C_{11}H_8O_2$	8	184
	6,7-dimethyl-1-tetralone	174	$C_{12}H_{14}O$	6	192
	3,3,4,5,7-pentamethyl-1-indanone	202	$C_{14}H_{18}O$	6	187
	3,3,5,6,7-pentamethyl-1-indanone	202	$C_{14}H_{18}O$	6	183
	4,5,8-trimethyl-1-tetralone	188	$C_{13}H_{16}O$	6	181
2.40	* 2-acetonaphthone	170	$C_{12}H_{10}O$	8	201
	2-hydroxy-1-naphthaldehyde	172	$C_{11}H_8O_2$	8	202.5
	2-allyl-4,5-dimethylphenol	162	$C_{11}H_{14}O$	5	191
	5,6-dimethyl-1-tetralone	174	$C_{12}H_{14}O$	6	197.5
	* 6-methoxy-1-tetralone	176	$C_{11}H_{12}O_2$	6	206.5
	1-naphthaldehyde	156	$C_{11}H_8O$	8	188
2.50	1,2,3,4-tetrahydro-8-isopropyl-2,5-dimethyl-1-naphthol	218	$C_{15}H_{22}O$	5	192.5
2.60	2-allyl-4,5-dimethylphenol	162	$C_{11}H_{14}O$	5	191
2.70	6-methyl coumarin	160	$C_{10}H_8O_2$	6	199.5
2.80	4(β-methylethylketo)phenol	164	$C_{10}H_{12}O_2$	5	

APE	Compound	MW	ELCOMP	R&DB	SPT
3.00					
	2,3-dihydroxynaphthalene	160	$C_{10}H_8O_2$	7	(a)
	2,7-dihydroxynaphthalene	160	$C_{10}H_8O_2$	7	(a)
3.20					
	2-hydroxy-2-methyl-1,4-naphthoquinone	188	$C_{11}H_8O_3$	8	213

(a) The compound does not elute off the Carbowax column within the temperature range of interest

* Compounds identified in diesel exhaust

Table H-2

Test Room Odor Evaluation of Oxygenated Reference Compounds

Compound	Conc. in Test Room (mg/M^3)	TIA	Odor Character
m-cresol	12.0	½	phenolic, irritation
2,3 dimethylphenol	0.4	½	tarry, solventy
3,5 dimethylphenol	0.4	½	burnt, sooty
2,6 dimethylphenol	0.4	½	medicinal, phenobic
3,4 dimethylphenol	0.4	)(	irritation
2,6 dimethoxyphenol	1.0	1	smoky, caramel
tetramethylphenol	1.0	1	hot wood
1 - methyl-4-isopropylphenol	1.0	½	metallic, burnt sweet
2 - methyl-5-isopropylphenol	0.1	½	sour, burnt, oily
allyldimethylphenol	1.0	)(	non recognizable
allylphenol	1.0	1	metallic
5-indanol	1.0	½-1	tarry naphthenate
tropolone	1.0	)(	sweet, musty
1 - naphthaldehyde	0.4	)(	pungency
2 - hydroxynaphthaldehyde	1.0	)(	irritation
terephthaldehyde	0.4	½	sour, irritation
4 - methylsalicylaldehyde	1.0	½	metallic, burnt wax
salicyladldehyde	0.4	)(	sweet, irritation
3,4 - dimethoxybenzaldehyde	0.4	½-1	burnt, pungent
p - methoxybenzaldehyde	0.4	½	burnt, pungent
2,4 - dihydroxybenzaldehyde	0.4	)(	irritation
2 - methyltetralone	0.5	½	particle feel, sooty
5 - methoxytetralone	1.0	½	particle feel, scorched
1 - methylcyclopentene ol-2-one-3(MCP)	0.1	½	burnt, sweet
nonylalchohol	0.1	½	oxidized oily
2 - nonenal	0.1	½	sour, oxidized oily

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